

Nanomaterials for 2D and 3D Printing

Nanomaterials for 2D and 3D Printing

Edited by Shlomo Magdassi and Alexander Kamyshny

WILEY-VCH

Editors

Prof. Shlomo Magdassi

The Hebrew University of Jerusalem
Casali Center for Applied Chemistry
Edmond J. Safra Campus
91904 Jerusalem
Israel

Dr. Alexander Kamyshny

The Hebrew University of Jerusalem
Casali Center for Applied Chemistry
Edmond J. Safra Campus
91904 Jerusalem
Israel

Cover: Background: fotolia/TASPP Pictures
in the circles are kindly provided by the editors.

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-33819-1
ePDF ISBN: 978-3-527-68582-0
ePub ISBN: 978-3-527-68580-6
Mobi ISBN: 978-3-527-68584-4
oBook ISBN: 978-3-527-68579-0

Typesetting SPi Global Private Limited, Chennai, India

Cover Design Grafik-Design Schulz

Printing and Binding

Printed on acid-free paper

Contents

List of Contributors *xiii*

1	Printing Technologies for Nanomaterials	1
	<i>Robert Abbel and Erwin R. Meinders</i>	
1.1	Introduction	1
1.2	Ink Formulation Strategies	4
1.3	Printing Technologies	6
1.3.1	Inkjet Printing	7
1.3.1.1	Toward 3D Printing	10
1.3.2	Laser-Induced Forward Transfer	11
1.3.2.1	Toward 3D Printing	13
1.3.3	Contact Printing Technologies	13
1.3.4	Photopolymerization	17
1.3.5	Powder Bed Technology	19
1.4	Summary and Conclusions	20
	References	20
2	Inkjet Printing of Functional Materials and Post-Processing	27
	<i>Ingo Reinhold</i>	
2.1	Introduction	27
2.2	Industrial Inkjet	28
2.3	Postprocessing of Metal-Based Inks for Conductive Applications	30
2.3.1	Mechanisms in Solid-State Sintering	32
2.3.2	Influence of Drying and Wet Sintering	34
2.3.3	Thermal Sintering	35
2.3.4	Chemical Sintering	35
2.3.5	Plasma Sintering	36
2.3.6	Sintering Using Electromagnetic Fields	37
2.3.6.1	Impulse Light Sintering	39
2.3.6.2	Microwave Sintering	40
2.3.6.3	Influence of the Substrate	41
2.4	Conclusion	42
	References	43

3	Electroless Plating and Printing Technologies	51
	<i>Yosi Shacham-Diamand, Yelena Sverdlov, Stav Friedberg, and Avi Yaverboim</i>	
3.1	Introduction	51
3.2	Electroless Plating – Overview	54
3.2.1	Electroless Plating – Brief Overview	55
3.3	Seed Layer Printing	57
3.4	Electroless Plating on Printed Parts	57
3.4.1	Methods and Approaches	59
3.4.1.1	Printed Pd Seed	59
3.4.1.2	Printed Ag Ink	60
3.4.1.3	Preseed Surface Modification	60
3.4.2	Electroless Metal Integration: Examples	60
3.5	Summary and Conclusions	63
	References	64
4	Reactive Inkjet Printing as a Tool for <i>in situ</i> Synthesis of Self-Assembled Nanoparticles	69
	<i>Ghassan Jabbour, Mutalifu Abulikamu, Hyung W. Choi, and Hanna Haverinen</i>	
4.1	Introduction to Reactive Inkjet Printing	69
4.2	RIJ of Self-Assembled Au NPs	70
4.3	Parameters Influencing the Growth of Au NPs	74
4.4	Simplifying the Approach (Single Cartridge) Using Single Cartridge Step	77
4.5	Further Progress toward Reduction of Fabrication Time (1 min)	77
4.6	Conclusion	79
	References	79
5	3D Printing via Multiphoton Polymerization	83
	<i>Maria Farsari</i>	
5.1	Multiphoton Polymerization	84
5.2	The Diffraction Limit	85
5.3	Experimental Setup	86
5.4	Materials for MPP	88
5.4.1	Introduction	88
5.4.2	Photoinitiators	88
5.4.3	Organic Photopolymers	89
5.4.4	SU-8	90
5.4.5	Hybrid Materials	90
5.4.6	Applications	91
5.4.6.1	Metamaterials	91
5.4.6.2	Biomedical Applications	94
5.5	Conclusions	96
	References	96

6	High Speed Sintering: The Next Generation of Manufacturing	107
	<i>Adam Ellis</i>	
6.1	The Need for the Next Generation of Additive Manufacturing	107
6.2	High Speed Sintering	109
6.3	Machine Setup & Parameter Control	109
6.4	Materials & Properties	112
6.5	HSS for High-Volume Manufacturing	113
6.6	Case Study: From Elite to High Street	115
6.7	Opening the Supply Chain	115
6.8	The Future of HSS and the Benefits of Inkjet	116
	References	116
7	Metallic Nanoinks for Inkjet Printing of Conductive 2D and 3D Structures	119
	<i>Alexander Kamyshny and Shlomo Magdassi</i>	
7.1	Introduction	119
7.2	Metallic Nanoinks: Requirements and Challenges	120
7.3	Synthesis and Stabilization of Metal NPs for Conductive Nanoinks	121
7.3.1	Synthesis	121
7.3.2	Stabilization	122
7.3.2.1	Stabilization Against Aggregation	122
7.3.2.2	Stabilization Against Oxidation	124
7.4	Formulation of Conductive Metallic Nanoinks	125
7.5	Formation of 2D Conductive Structures: Printing and Sintering	127
7.6	3D Printing of Conductive Patterns: Formation and Sintering	134
7.7	Applications of Metallic Inkjet Nanoinks in Printed Electronics	135
7.7.1	RFID Tags	136
7.7.2	Thin-Film Transistors	136
7.7.3	Electroluminescent Devices and Light-Emitting Diodes	136
7.7.4	Transparent Conductive Electrodes	137
7.7.5	Organic Solar Cells	138
7.8	Outlook	139
	References	140
8	Graphene- and 2D Material-Based Thin-Film Printing	161
	<i>Jiantong Li, Max C. Lemme, and Mikael Östling</i>	
8.1	Introduction	161
8.2	Printing Procedures	162
8.2.1	Ink Formulations	162
8.2.2	Jetting and Patterns	166
8.2.3	Drying	166

8.2.4	Posttreatments	171
8.3	Performance and Applications	172
8.3.1	Transparent Conductors	173
8.3.2	Micro-Supercapacitors	173
8.3.3	Photodetectors	174
8.3.4	Solar Cells	176
8.4	Discussion and Outlook	177
	Acknowledgments	178
	References	178
9	Inkjet Printing of Photonic Crystals	183
	<i>Minxuan Kuang and Yanlin Song</i>	
9.1	Introduction	183
9.2	Inkjet Printing of Photonic Crystals	184
9.2.1	Process of Inkjet Printing	184
9.2.2	Inkjet Printing of Fine Controlled PC Dots and Lines	186
9.2.2.1	Influence of the Ink Formulation	186
9.2.2.2	Influence of Substrate Wettability	188
9.2.2.3	Suppression of “Coffee-Ring” Effect	193
9.3	Application of Printing of Photonic Crystals	196
9.3.1	Photonic Crystal Patterns	196
9.3.2	Printing Patterned Microcolloidal Crystals with Controllable 3D Morphology	199
9.3.3	Inkjet-Printed PCs Applied in Vapor Sensors	201
9.3.4	Inkjet-Printed PCs Applied in Chemical Detection	201
9.4	Outlook	203
	References	204
10	Printable Semiconducting/Dielectric Materials for Printed Electronics	213
	<i>Sunho Jeong and Jooho Moon</i>	
10.1	Introduction	213
10.2	Printable Materials for Semiconductors	213
10.3	Printable Materials for Dielectrics	219
10.4	Conclusions	223
	References	224
11	Low Melting Point Metal or Its Nanocomponents as Functional 3D Printing Inks	229
	<i>Lei Wang and Jing Liu</i>	
11.1	Introduction of Metal 3D Printing	229
11.2	Low Melting Point Metal Ink	230
11.2.1	Liquid Metal Printing Ink	230
11.2.2	Nanoliquid Metal	232

11.3	Liquid-Phase 3D Printing	234
11.3.1	Fabrication Scheme	234
11.3.2	Forming Principle of Metal Objects in Cooling Liquid	235
11.3.3	Liquid-Phase Printing of Metal Structures	236
11.3.4	Factors Affecting the Printing Quality	237
11.3.5	Comparison Between Liquid-Phase Cooling and Gas-Phase Cooling	238
11.3.6	Vision of the Future Liquid-Phase Printing	240
	Acknowledgment	241
	References	241
12	Inkjet Printing of Conducting Polymer Nanomaterials	245
	<i>Edward Song and Jin-Woo Choi</i>	
12.1	Introduction	245
12.2	Inkjet Printing of Polyaniline Nanomaterials	246
12.2.1	Introduction	246
12.2.2	Chemical Structure, Electrochemical Properties, and Conductivity of Polyaniline	246
12.2.3	Inkjet-Printed Polyaniline Nanomaterials	249
12.2.4	Applications of Inkjet-Printed Polyaniline Nanomaterials	250
12.3	Polypyrrole	251
12.3.1	Properties and Synthesis of Polypyrrole (Ppy) Nanomaterials	251
12.3.2	Inkjet Printing and Applications of Ppy Nanomaterials	254
12.4	Polythiophene (Pth) and Poly(3,4-Ethylenedioxythiophene) (PEDOT)	258
12.4.1	Properties and Synthesis of Pth and PEDOT Nanomaterials	258
12.4.2	Inkjet Printing and Applications of Pth Nanomaterials	258
12.5	Conclusions and Future Outlook	258
	References	260
13	Application of Printed Silver Nanowires Based on Laser-Induced Forward Transfer	265
	<i>Tepei Araki, Rajesh Mandamparambil, Jinting Jiu, Tsuyoshi Sekitani, and Katsuaki Suganuma</i>	
13.1	Introduction	265
13.2	Ag NW Transparent Electrodes	266
13.2.1	Background	266
13.2.2	Transparent Electrodes Formed from Ultra-Long Ag NWs	267
13.3	Printed Ag NW Electrodes	269
13.3.1	Fabrication and Properties of Stretchable Electrodes	269
13.3.2	Ag NWs Printing by LIFT	269
13.4	Summary	271
	References	271

14	Inkjet Printing of Functional Polymers into Carbon Fiber Composites	275
	<i>Patrick J. Smith, Elliot J. Fleet, and Yi Zhang</i>	
14.1	Inkjet Printing	275
14.2	Carbon Fiber Composites	276
14.3	Mechanical Tests	276
14.4	Printing and Sample Preparation	277
14.5	Carbon Fiber Composites that Contain Inkjet-Printed Patterns Composed of PMMA Microdroplets	278
14.6	Carbon Fiber Composites that Contain Inkjet-Printed Patterns Composed of PMMA and PEG Microdroplets	283
14.7	Morphology of the Printed PMMA and PEG Droplets	284
14.8	Printed Polymers for Intrinsic Repair of Composites	286
14.9	Conclusions	288
	Acknowledgments	289
	References	289
15	Inkjet-Printable Nanomaterials and Nanocomposites for Sensor Fabrication	293
	<i>Niamh T. Brannelly and Anthony J. Killard</i>	
15.1	Introduction	293
15.2	Metallic Inks	294
15.2.1	Gold	294
15.2.2	Silver	296
15.2.3	Copper, Nickel, and Alumina	296
15.2.4	Metal Oxides	297
15.3	Conductive Polymers	298
15.3.1	Polyaniline	299
15.3.2	Polypyrrole	300
15.3.3	Prussian Blue	301
15.3.4	PEDOT	302
15.4	Carbon Nanomaterials	302
15.4.1	Graphene Oxide	302
15.4.2	Carbon Nanotubes	304
15.5	Future Outlooks and Conclusions	308
	References	308
16	Electrochromics for Printed Displays and Smart Windows	317
	<i>Pooi See Lee, Guofa Cai, Alice L.-S. Eh, and Peter Darmawan</i>	
16.1	Overview on Electrochromics	317
16.1.1	Electrochromics for Green Buildings	318
16.1.2	Electrochromics for Displays	320
16.1.2.1	Solution Processing of Electrochromics	322
16.1.2.2	Printing Techniques in Electrochromics	324
16.2	Screen Printing	324
16.3	Inkjet Printing	326

16.4	Flexographic Printing	329
16.5	Roll-to-Roll Printing	329
16.6	Other Printing Methods	329
16.7	Conclusions and Perspectives	330
	References	332
	Index	341

List of Contributors

Robert Abbel

TNO, Equipment for Additive
Manufacturing (EfAM)
De Rondon 1
5612 AP Eindhoven
The Netherlands

Mutalifu Abulikamu

School of Electrical Engineering
and Computer Science
University of Ottawa, and Centre
for Research in Photonics
Advanced Research Complex
Ottawa, ON
Canada

Teppeï Araki

Osaka University
The Institute of Scientific and
Industrial Research
8–1 Mihogaoka
Ibaraki, Osaka 5670047
Japan

Niamh T. Brannelly

University of the West of England
Bristol BS16 1QY
UK

Guofa Cai

Nanyang Technological University
School of Materials Science and
Engineering
50 Nanyang Avenue
Singapore 639798
Singapore

Hyung W. Choi

University of Cambridge
Engineering Department
Trumpington Street
Cambridge CB2 1PZ
United Kingdom

Jin-Woo Choi

Louisiana State University
School of Electrical Engineering and
Computer Science
3101 Patrick F. Taylor Hall
Baton Rouge, LA 70803
USA

Peter Darmawan

Nanyang Technological University
School of Materials Science and
Engineering
50 Nanyang Avenue
Singapore 639798
Singapore

Alice L.-S. Eh

Nanyang Technological University
School of Materials Science and
Engineering
50 Nanyang Avenue
Singapore 639798
Singapore

Adam Ellis

The University of Sheffield
Department of Mechanical
Engineering
Mappin Street
Sheffield
South Yorkshire S1 3JD
UK

Maria Farsari

IESL-FORTH
N. Plastira 100
70013 Heraklion
Crete
Greece

Elliot J. Fleet

NetComposites Ltd.
Chesterfield
Derbyshire
UK

Stav Friedberg

Tel-Aviv University
Department of Physical Electronics
69978 Ramat-Aviv
Tel-Aviv
Israel

Hanna Haverinen

School of Electrical Engineering
and Computer Science
University of Ottawa, and Centre
for Research in Photonics
Advanced Research Complex
Ottawa, ON
Canada

Ghassan Jabbour

School of Electrical Engineering
and Computer Science
University of Ottawa, and Centre
for Research in Photonics
Advanced Research Complex
Ottawa, ON
Canada

Sunho Jeong

Division of Advanced Materials
Korea Research Institute of Chemical
Technology (KRICT)
141 Kajeong-ro, Yuseong-gu
Daejeon 305-600
Republic of Korea

Jinting Jiu

Osaka University
The Institute of Scientific and
Industrial Research
8-1 Mihogaoka
Ibaraki
Osaka 5670047
Japan

Alexander Kamyshny

The Hebrew University of Jerusalem
Casali Center of Applied Chemistry,
Institute of Chemistry
Edmond J. Safra Campus
91904 Jerusalem
Israel

Anthony J. Killard

University of the West of England
Bristol BS16 1QY
UK

Minxuan Kuang

Key Laboratory of Green Printing,
Chinese Academy of Sciences,
and Engineering Research Center of
Nanomaterials for Green Printing
Technology
Institute of Chemistry
Zhongguancun North First Street 2
Beijing 100190
China

Pooi S. Lee

Nanyang Technological University
School of Materials Science and
Engineering
50 Nanyang Avenue
Singapore 639798
Singapore

Max C. Lemme

KTH Royal Institute of Technology
School of Information and
Communication Technology
Electrum 229
16440 Kista
Sweden

and

University of Siegen
Department of Electrical Engineering
and Computer Science
Hölderlinstr. 3
57076 Siegen
Germany

Jiantong Li

KTH Royal Institute of Technology
School of Information and
Communication Technology
Electrum 229
16440 Kista
Sweden

Jing Liu

Chinese Academy of Sciences
Technical Institute of Physics and
Chemistry
29 Zhongguancun East Road
Haidian District
Beijing, 100190
China

Shlomo Magdassi

The Hebrew University of Jerusalem
Casali Center of Applied Chemistry
Institute of Chemistry and The Center
for Nanoscience and Nanotechnology
Edmond J. Safra Campus
91904 Jerusalem
Israel

Rajesh Mandamparambil

Technische Universiteit Eindhoven
TNO Industrie
De Rondom 1
5612 AP Eindhoven
The Netherlands

Erwin R. Meinders

TNO
Equipment for Additive
Manufacturing (EfAM)
De Rondom 1
5612 AP Eindhoven
The Netherlands

Jooho Moon

Yonsei University
Department of Materials Science and
Engineering
50 Yonsei-ro, Seodaemun-gu
Seoul 120-749
Republic of Korea

Mikael Östling

KTH Royal Institute of Technology
School of Information and
Communication Technology
Electrum 229
16440 Kista
Sweden

Ingo Reinhold

Xaar Jet AB
Advanced Manufacturing Techn.
Elektronikhöjden 10
175 26 Järfälla
Sweden

Tsuyoshi Sekitani

Osaka University
The Institute of Scientific and
Industrial Research
8–1 Mihogaoka
Ibaraki
Osaka 5670047
Japan

Yosi Shacham

Tel-Aviv University
Department of Physical Electronics
69978 Ramat-Aviv
Tel-Aviv
Israel

Patrick J. Smith

University of Sheffield
Department of Mechanical
Engineering
Yorkshire
UK

Edward Song

University of New Hampshire
Department of Electrical and
Computer Engineering
Durham, NH
USA

Yanlin Song

Key Laboratory of Green Printing,
Chinese Academy of Sciences,
and Engineering Research Center of
Nanomaterials for Green Printing
Technology
Institute of Chemistry
Zhongguancun North First Street 2
Beijing 100190
China

Katsuaki Suganuma

Osaka University
The Institute of Scientific and
Industrial Research
8–1 Mihogaoka
Ibaraki
Osaka 5670047
Japan

Yelena Sverdlov

Tel-Aviv University
Department of Physical Electronics
69978 Ramat-Aviv
Tel-Aviv
Israel

Lei Wang

Chinese Academy of Sciences
Technical Institute of Physics and
Chemistry
29 Zhongguancun East Road
Haidian District
Beijing, 100190
China

Avi Yaverboim

Tel-Aviv University
Department of Physical Electronics
69978 Ramat-Aviv
Tel-Aviv
Israel

Yi Zhang

University of Sheffield
Department of Mechanical
Engineering
Yorkshire
UK

Printing Technologies for Nanomaterials

Robert Abbel and Erwin R. Meinders

1.1 Introduction

For centuries, printing of texts and graphics on flat (two-dimensional) substrates such as textiles and paper has been an essential enabling technology for the cultural development of mankind. Only recently has this technique been considered as a valuable tool for the processing of functional nanomaterials, for example, in the electronics and biomedical industries [1–6]. For electronics manufacturing, for example, printing has some decisive advantages compared with the more traditional approaches of semiconductor processing. First of all, printing is an additive process, meaning that functional materials are deposited only where needed and can be used much more efficiently than with subtractive techniques, which tend to produce a lot of waste [7, 8]. In addition, printing can be carried out at atmospheric pressure, making high-vacuum technologies obsolete, which also contributes to significant savings on production costs. A third advantage is the selectivity of printing, making multimaterial applications such as multicolor lighting [9–11] or printed thin-film transistors [12, 13] possible. Since in the graphics printing industry, many 2D printing technologies have already been developed toward roll-to-roll processing, commercial mass production of nanomaterial-based printed electronics devices in a continuous manufacturing mode is also within reach [14–16].

A wide variety of 2D printing technologies has been applied for the processing of functional nanomaterials, which can be subdivided into two different groups: noncontact or digital (maskless) printing technologies (without physical contact between printing equipment and substrate) and contact (mask-based) printing technologies (with physical contact). In noncontact printing, droplets or jets of the functional ink are generated at a (small) distance from the substrate and transferred onto it by a pressure pulse that propels them across the interspace. Contact printing typically makes use of a predetermined pattern, embedded as a mask in a drum or screen, which is repeatedly replicated on the substrate by directly touching it. Typical examples for noncontact techniques are inkjet printing (IJP) and laser-induced forward transfer (LIFT), and examples of contact technologies are offset, flexo, gravure, screen, and microcontact printing.

In general, critical issues to be considered during the choice for a specific printing technology for functional nanomaterials are technical aspects such as resolution, feature definition, adhesion, process reliability and stability, manufacturing speed, and device performance. Also nontechnical process features such as production volume and cost, environmental impact, and operator and customer safety are important, since all of these combined will determine whether printing will be a technically and economically viable option for a specific type of device. Since functional electronic and biomedical devices are frequently composed of complex ultrathin stacks of various (nano)materials, some of which can be highly sensitive to mechanical pressure, contactless printing can be a decisive advantage [17]. The balance between design flexibility and the potential for mass manufacturing is another consideration. Digital printing technologies offer a lot of design freedom and easily allow for image adjustments to compensate for possible substrate deformations (for instance, in the case of flexible or stretchable substrates [18]). However, productivity should come from mass parallelization with the obvious challenges such as yield, stability, reproducibility, and durability.

By contrast, all contact printing techniques involve some kind of physical stencil that determines the printing pattern and needs to be adjusted every time a different image is to be produced. This feature, in combination with its potential for very-high-throughput production, makes many contact printing techniques especially suited for the production of large numbers of identical devices [15]. In mature industrial production processes, contact printing is therefore usually preferred, unless possible damage to the products by mechanically touching the surface prohibits its use. By contrast, noncontact processes are generally the technology of choice where small series are required, such as in many academic research laboratories and in early-stage industrial research and development. However, the potential for scalability or transfer to other processes, which are more adept for mass production, is required for the latter to be of any practical use.

In addition to nanomaterials' deposition in two dimensions on flat substrates, functional printing has recently also been applied for the construction of three-dimensional objects [6, 19, 20]. 3D printing or additive manufacturing (AM) is known as a layer-by-layer manufacturing technology to build 3D products. In analogy to 2D technologies, it is an enabling approach with numerous advantages compared with the conventional (subtractive) manufacturing technologies. AM enables the cost-effective manufacturing of complex, personalized, and customized products. It also offers the possibility to introduce multimaterial products or parts with material gradients [21]. AM integrates very well with design tools and computer-aided design (CAD) software and as a result, the AM approaches can significantly impact both time and cost savings, as well as inventory, supply chain management, assembly, weight, and maintenance. AM is seen as an enabling technology for many applications, such as embedded and smart integrated electronics (Internet of things, smart conformal and personalized electronics [22]), complex high-tech (sub)modules made of ceramic or metal with multimaterial or grading material properties [23], and human-centric products (e.g., dentures, prostheses, implants [6, 24]). While new materials and manufacturing technologies are introduced in the market, we see that for

many applications the technology is still immature: product quality is inferior to that obtained with conventional methods, the choice of available materials is limited, yield is low by process-induced defects, manufacturing costs are high, and production speeds are typically low [25].

3D printing comes in various embodiments. Selective deposition techniques, such as viscous jetting, fused deposition modeling, cladding, or wire feed are well-known technologies based on the consecutive deposition of a printable/processable (nano)material to build layer-by-layer the 3D product. The product definition is determined by the spatial deposition and the dimensional stability of the deposited material (the material needs to have fluidic properties during the release from the reservoir or nozzle to print but should have (rigid and) superior material properties in the final product), and the patterning resolution of the deposition heads. The other class of AM technologies is based on pattern definition with an external source (e.g., laser beam or E-beam) in a homogeneous layer of material. During each print step, a homogeneous layer of material is deposited, but only the fraction that constitutes the final product is fused to the part via a sintering process (selective laser sintering (SLS)), melting process (selective laser melting (SLM)), binder jetting process, or photopolymerization process (stereolithography (SLA), vat photopolymerization). This family of AM technologies comes often with a higher spatial resolution but frequently suffers from inferior material properties (porosity in SLS, defects in SLM, uncured monomers and inferior material properties in vat). Emerging technologies are combinations of these: two-photon, reactive jetting, conformal printing, and so on.

The current focus for metal AM is on monomaterial technology improvement to enable lightweight parts for space, aerospace, and automotive applications and customized parts for medical and high-tech. The currently utilized processes are mainly based on cladding or selective melting (with laser or e-beam) to make metallic parts from powder. Challenges include the avoidance of thermally induced stresses that give rise to warpage and mechanical deformation, homogeneity and purity of the printed part, and defectivity control (e.g., small defects might result in fatigue challenges).

The currently utilized technology for ceramics parts is selective sintering: the fusion of ceramics particles under the influence of heat or photopolymerization based on a polymer binder system, in which a ceramics powder is dispersed. In both cases, the final ceramic product is preferably 100% pure and does not comprise contaminants of the binder.

Nanomaterials are typically used in both 2D and 3D printing to add functionality to the polymer or multimaterial systems. Nanomaterials can be added to a polymer system to improve material properties (e.g., mechanical strength, color, flame-retardation ability, biocompatibility), or to create anisotropy (via fibers, filaments, nanotubes, etc.). Examples include the addition of clay particles to photoresins to improve the mechanical properties such as impact strength and biocompatibility for use in high-tech engineering. Another example is the addition of metal compounds, such as metal nanoparticles, to make conductive tracks in free-form electronics applications.

1.2 Ink Formulation Strategies

The core ingredient of an electronic or biomedical ink is the functional nanomaterial to be deposited. Since a detailed overview is presented in Chapters 7–14, here only a brief summary is given. A wide variety of nanomaterials with all kinds of properties and shapes have been formulated into inks and pastes. Examples include conductive [26], semiconductive (e.g., electroluminescent or photovoltaic [27]), or piezoelectric [28] as well as catalytically and biologically active materials [29]. Also the dimensions of the materials used cover the entire range defined for nanotechnology from the sub-nanometer regime up to fractions of a micrometer. “Zero-dimensional” objects such as nanoparticles of spherical, but also other shapes have been processed [26], as well as more complex shapes such as rods and wires [27], sheets [30, 31], and complex three-dimensional architectures [32, 33]. Apart from functional nanomaterials consisting of a single component, more complex nano-objects have also been reported as functional ink ingredients [34]. In accordance with this wide variety of materials and functionalities, the technical applications also represent the entire range of devices such as sensing, energy conversion, communication and logic, lighting, and catalysis. For specific examples, the reader is referred to Chapters 15–16 of this book.

Ink formulation requires a delicate balance between the desired functional properties in the device after deposition and postprocessing, and printability. To achieve good printability, precise control over a number of ink properties is necessary, such as viscosity, stability, wettability, and drying behavior.

In all ink formulations, the functional nanomaterials are dispersed in some kind of fluid carrier, which can be a pure solvent or a mixture and has the function to allow processing from the liquid state. The choice for a particular solvent system depends on a variety of considerations, such as compatibility with the nanomaterials and the intended substrate, envisioned processing conditions, and intended application. For large-scale production, cost, environmental, and health issues also need to be taken into account.

Pure dispersions of nanomaterials in liquids usually are not stable and thus cannot be properly deposited by printing technologies. For example, nanoparticles strongly tend to cluster, agglomerate, and precipitate, due to their high surface energies, which in turn leads to altered rheological properties, an uneven distribution of the material, or an increased surface roughness after printing. Dispersants are, therefore, typically used to stabilize the nanoparticles (see [35] for a theoretical study and [36–38] for practical examples). These compounds are typically neutral or electrically charged organic molecules or polymers. They cause reciprocal repulsion when adsorbed on the particle surfaces, thereby preventing the formation of larger aggregates. Also, pH and electrolyte concentration can influence the dispersion stability of the nanoparticles because of their influence on the zeta-potentials. pH can be controlled by the addition of a buffer system. For biological functional components, pH control is especially important, since proteins tend to denature upon pH changes, thereby losing their functionality [39].

Ink stability during storage is another demanding requirement. In addition to agglomeration and settling of particles, as described earlier, evaporation of

solvents may lead to a change in ink composition and an increasing concentration of nanomaterials, which in turn impacts printability. Lifetime stability can be increased by high-boiling-point solvents. Another possibility is the addition of humectants, which bind the solvent components, thereby lowering their tendency to evaporate [40]. Typical examples are polymers with polar side groups, which attract polar solvents, especially water.

Ink rheology (e.g., viscosity or shear thinning behavior) impacts printability and needs to be adapted for each deposition technology. Ink viscosity can, for instance, vary from 2 mPa s (water-like inks typical for IJP) to above 300 Pa s (very thick pastes for screen printing). Ink viscosity can be controlled by concentration of the functional nanomaterials, viscosity of the carrier liquid, and additional ink ingredients. The optimum amount of dispersed particles is typically determined by the printing method. Viscosity modifiers such as high-molecular-weight polymers, gelators, or lower viscosity solvents can be added to achieve the desired viscosity, and some of them are also useful to induce shear thinning behavior by chain alignment or reversible network collapse under shear stress.

Controlling an ink's surface tension is another crucial step when formulating an ink. During the printing processes, the material will become deformed. This degree of deformation and the force necessary to achieve it are determined by several factors, one of which is surface tension. Lowering an ink's surface tension is usually rather easily achieved by the addition of small amounts of surface-active molecules, which tend to accumulate at the interfaces. A more extensive reformulation such as replacement of the main solvent is usually necessary if an ink's surface tension is too low.

In addition, the wetting behavior of an ink on a substrate after deposition is also influenced by its surface tension. A variety of substrate materials are used in functional printing, from glasses and semiconductor wafers to plastic foils, papers, and textiles. Accordingly, a wide range of varying surface properties is encountered, defined by the material and its surface chemistry and topology (e.g., roughness, porosity, possible anisotropy, prepatterning). In addition, surface chemistries can be tuned by the application of coatings and other surface treatment methods, such as exposure to reactive plasmas or ozone [41]. This wide range of surface properties needs to be taken into account during ink formulation, since only an appropriate combination of substrate and ink characteristics will result in the formation of well-defined printed patterns [42]: very strong repulsive interactions generally give rise to the formation of isolated droplets instead of continuous structures, whereas very strong attractive interactions will result in wide spreading, thereby limiting feature resolution. In order to print well-defined, fine, and continuous functional structures, usually a regime of intermediate wetting is preferred. Good or even complete wetting, however, can be useful when large areas need to be coated with a homogeneous continuous film of functional materials. Chemical compatibility with the substrate or coating material is also an important factor for the selection of ink ingredients, since chemical reactions between substrate and ink or the dissolution of the surface coating are usually undesired.

Postprocessing steps are typically applied to improve the functional performance of the deposited nanomaterials, for instance, exposure to heat to remove

the solvents and additives. These steps can also be controlled by adjusting the ink composition. Especially, inks with low nanomaterial loads, high solvent contents, and low viscosities exhibit complex flow patterns during solvent evaporation, which tend to accumulate the solid functional nanomaterials at the edges of the structures, giving rise to the so-called “coffee ring effect”. These irregular height profiles can aggravate further processing and compromise device performance, for example, when very thin continuous films need to be deposited on top. This can be avoided by designing complex solvent mixtures composed of ingredients with different boiling points (and thus sequential evaporation), thereby causing continuous compositional changes in the ink, or by choosing appropriate drying conditions [43, 44].

Evaporation of the solvent may also lead to deterioration of the wetting properties of an ink. Although under special circumstances, this effect can be exploited to create well-defined, extremely thin lines with high aspect ratios [45], it is usually detrimental and therefore unwanted. The drying process can obviously be influenced by the choice of volatile components in the ink, but in addition, specific interactions between the various solvents and other ink ingredients need to be taken into account. Nonvolatile compounds with high affinity to one or several of the solvents, for example, added as humectants or dispersants, can retard evaporation, giving rise to different transient ink compositions during the drying process.

After treatment, proper functionality of an ink deposit is frequently closely related to its topology and internal structure. Solvent loss and the decomposition of organic components such as stabilizers usually result in a significant volume shrinkage, which can result in crack formation and a rough surface profile. Similar damage can also occur from mechanical stress when flexible or stretchable devices are prepared. These phenomena can cause partial material disintegration, structural defects, and incomplete adhesion of possible consecutive layers. Achieving good cohesion within a dried ink structure is, therefore, crucial for the ultimate device performance and can be achieved by the addition of binders, which keep the structures together. In the specific case of electrically conductive inks based on metal nanoparticles, special “sintering agents” have been added, promoting nanoparticle merging during the drying process [46].

Another aspect of ink functionality is its adhesion to the underlying surface, since delamination can seriously affect final device performances. Typically, nanomaterials do not exhibit good adhesion to common substrate materials such as glass or plastic foils. To improve binding properties, polymeric binders and specific bifunctional adhesion promoters can be added with high affinities to both substrate and functional ink components. Typical examples include molecules containing silane groups, which can easily bind to glass, and thiol groups, which have a strong affinity toward certain types of metals, which by themselves do not adhere well on glass [47, 48].

1.3 Printing Technologies

Noncontact printing technologies typically deposit the ink in the form of free flying droplets formed at some distance from the substrate. The two most important

noncontact printing technologies are IJP [42] and LIFT [49]. Whereas IJP is a well-established technology, LIFT is a rather new development specifically aimed at high-resolution printing of high-viscous and solid materials. Aerosol patterning is another type of noncontact printing [50]. Heat is used to create airborne nanoparticles that are directed to a substrate via a confined jet. An annulus of air is used to control the dimensions of the deposited material.

As outlined earlier, noncontact printing combines the key advantages of being compatible with mechanically sensitive substrates and digital patterning. This means that both technologies offer a high flexibility of design, since an adjustment in the digital printing pattern will directly be reflected in a different printed structure. As a consequence, a freedom of design is achieved that is not easily equaled by other approaches and can be especially advantageous when batches of limited numbers of identical functional devices are produced.

1.3.1 Inkjet Printing

IJP is characterized by the formation of droplets by a sudden pressure pulse in the nozzle chamber. In order to leave the nozzle in a reliable manner and to allow fast droplet generation (high printing frequencies), inkjet inks generally have low viscosities (in the order of 2–50 mPa s) and rather low solid contents. At least two types of IJP are distinguished, depending on the manner of droplet formation and ejection, which can be achieved either by a heat pulse, inducing solvent boiling and thus a pressure pulse (thermal IJP), or by the shape change of a piezoelement integrated in the nozzle chamber walls (piezoelectric IJP) (Figure 1.1). In both cases, the pressure pulse is eventually the result of an electric voltage pulse, which can be modulated in terms of intensity, time duration, and voltage ramp in order to optimize the ejection process. Since the exact pulse shape will influence printing parameters such as reliability, droplet size, and speed and printing stability, this so-called waveform tuning is of crucial importance during printing parameter optimization [51–53].

Due to the surface tension of the ink, during flight, the formed jet will contract into a single spherical droplet or will break up into a number of individual droplets, some of which might merge into one main droplet, while others will remain as so-called satellite droplets (Figure 1.1) [54]. The latter ones are unwanted, because they tend to diminish the definition of the printed pattern by landing outside the designated area. An important part of waveform optimization is, therefore, to avoid satellite droplet formation.

A number of phenomena can occur when droplets hit the surface. First of all, the physical interactions between the substrate surface and the ink are important, which are governed by the ink composition, the physical properties of the substrate, and the impact velocity. An ink droplet hitting the surface at too high speed will splash and create a very ill-defined pattern. Waveform tuning can control impact velocity and avoid the occurrence of splashing. After deposition, the shape of ink droplets on a substrate is determined by the former's surface tension and the latter's surface free energy. A measure for this interaction is the contact angle, that is, the angle formed between the substrate and the ink droplet. Very high contact angles indicate unfavorable interactions and a high degree of repulsion. Under these conditions, it is usually difficult to obtain

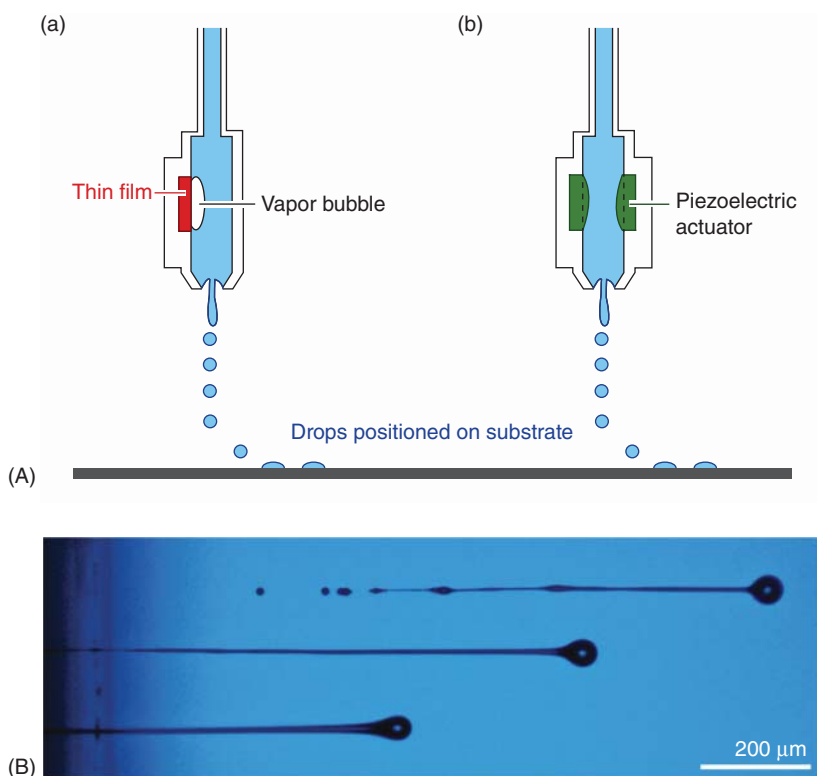


Figure 1.1 Operational principles of thermal and piezoelectric inkjet printing (A) and jet break up and satellite formation during the inkjet process (B). (Derby (2010) [42]. Reproduced with permission of Annual Reviews.)

continuous functional (e.g., electrically conductive) structures, since any printed line will have a high tendency to break up into individual, unconnected droplets (dewetting). On the contrary, very low contact angles lead to complete wetting, that is, there are strong attractive interactions between ink and substrate, and thus a high contact area between both is thermodynamically favored. Too strong wetting can lead to extreme spreading of the ink, thus preventing any fine details to be formed. For high-resolution functional patterns, an intermediate wetting regime is usually optimal. It can be achieved by either modifications to the ink formulation, for example, by lowering its surface tension, or by changing the surface chemistry of the substrates, for example, by coatings or plasma treatments [55, 56]. Furthermore, for a given ink–substrate combination, the quality of the printed features can be additionally controlled by adjusting the printing parameters such as substrate temperature, droplet spacing, and jetting frequency (Figure 1.2) [57].

The drying process has also a major influence on the final properties of an ink-jetted pattern. Because of the low viscosities and high solvent contents of inkjet inks, transport phenomena occur on a larger scale than in more paste-like functional inks.

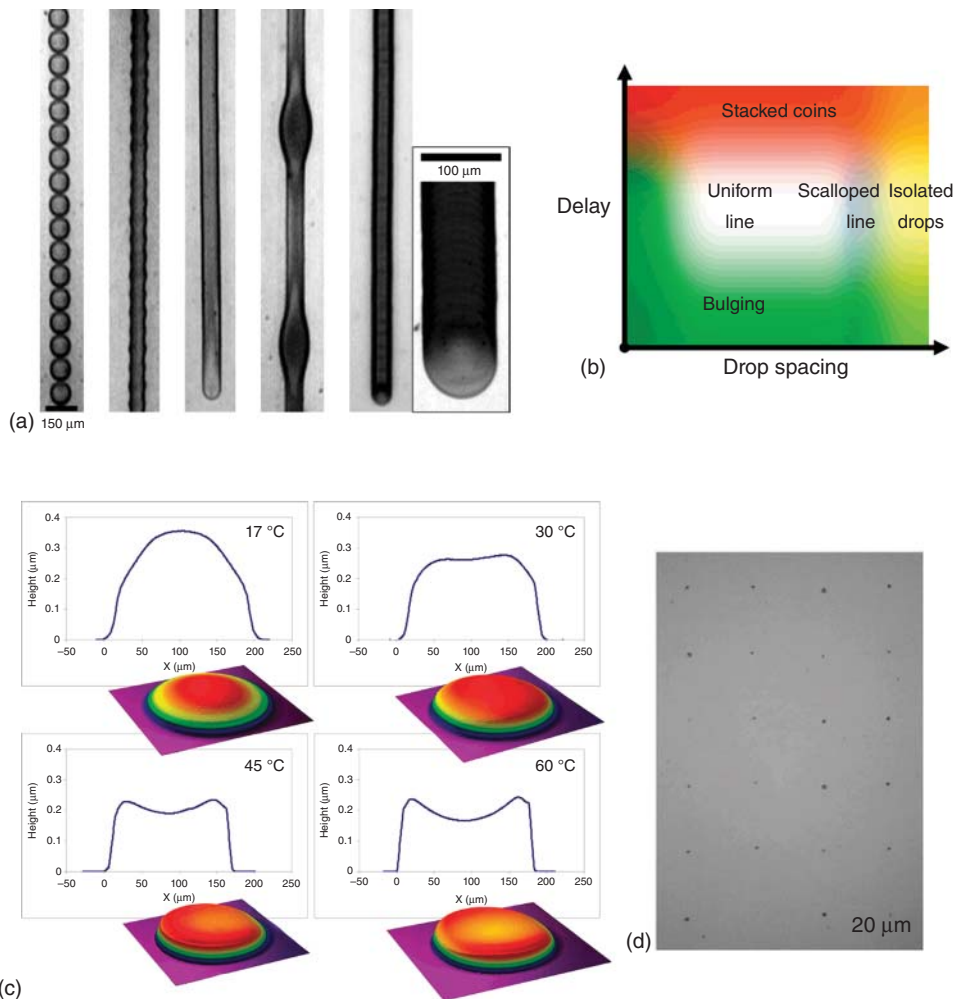


Figure 1.2 Effect of drop spacing and deposition delay on definition of inkjet-printed lines (a,b) and effect of drying temperature on surface profiles of inkjet-printed droplets (c). (Soltman and Subramanian (2008) [57]. Reproduced with permission of American Chemical Society.) Array of micrometer-sized droplets of a nickel nanoparticle ink deposited by electrostatic IJP (d). (Ishida *et al.* (2007) [58]. Reproduced with permission of Japan Society of Applied Physics.)

Due to wetting, line widths achievable by IJP are usually limited to a minimum of 20 μm , unless specific measures are taken such as pre patterning of the substrate surface. Also, it is possible to reduce the droplet sizes, but a reduced process speed is usually the consequence. The typically low solid contents of inkjet inks result in high volume shrinkage during drying, which means that (average) line thicknesses after processing are in the order of a few micrometers at most. Multiple layer printing offers a solution but has its own specific challenges, such as interlayer alignment, instabilities of multiple wet-stacked ink layers, or different

wetting behavior of the ink on a predried layer than on the substrate. Another possibility is to increase the resolution, which means to increase the droplet density to be deposited, but this can also lead to a collapse of the high wet lines. In addition, both approaches to higher structures are directly related to a lower printing speed.

Electrostatic IJP is a variety of “classic” IJP, where the droplet is not produced by a pressure pulse but by an electric field between the nozzle tip and the substrate [59]. Very small droplet volumes can be achieved with this technology, allowing extremely fine structures to be deposited. Drop sizes on the substrate of below 1 μm have been demonstrated (Figure 1.2) [58]. In addition, the electric field also serves to guide the droplet toward the substrate, thereby limiting deviations and increasing positioning accuracy. This is especially important for small droplets, which tend to stray away more strongly from a straight trajectory than do larger droplets. In contrast to classic IJP, electrostatic IJP is also compatible with inks of higher viscosities. A major drawback for industrial mass production at current state is its incompatibility with high production speeds and large-area fabrication.

1.3.1.1 Toward 3D Printing

Viscous jetting technologies come in different embodiments. Material can be liquefied by heating it up to above the melting temperature to squeeze it through nozzles and to form voxels on the target substrate. Examples include thermal wax, polymer, and metal. Polymer systems can go to 300–400 °C, while metal printing can go well above the 1000–1500 °C range. The jetted materials reach the substrate in a molten or fluidic state, causing, in combination with the wetting properties of the surface and previously built layers/parts, the voxel to spread out, thereby limiting the resolution and pattern definition. A key advantage is the recovery of the material properties after solidification.

Different nozzle systems have been developed. TNO has developed a jetting system for high-viscous material systems. The technology is based on the Plateau–Rayleigh instability to create a steady stream of well-defined droplets. The instability is induced by the design of the nozzle in combination with a piezo perturbation [60]. The system showed the capability to create 40–50 μm voxels in the case of metal (Sn, Au, and Ag) and polymer systems. Several methods have been introduced for droplet on demand applications, for instance, by mechanical or electrical removal of the redundant droplets/voxels.

An image of the high-viscosity jetting head of TNO is given in Figure 1.3. Jetting systems are ideal for multimaterial applications, where different nozzles can feed different materials to the build. Challenges include material interface instability, material compatibility, and unwanted mixing.

A related application is the formation of monodisperse particles (powders) via well-defined cooling or drying of the dispersed droplets. The technology was successfully applied to the formation of metal powder (via immersion in a cooling liquid) and to the formation of milk powder and fine chemistry products (via conditioned cooling in air) [61]. A proof-of-concept study of a multinozzle system with internal filtration was executed by TNO. IJP was also applied for low-temperature 3D metal microstructure fabrication of metal nanoparticles [62]. Metal nanoparticle inks were successfully deposited via IJP to create

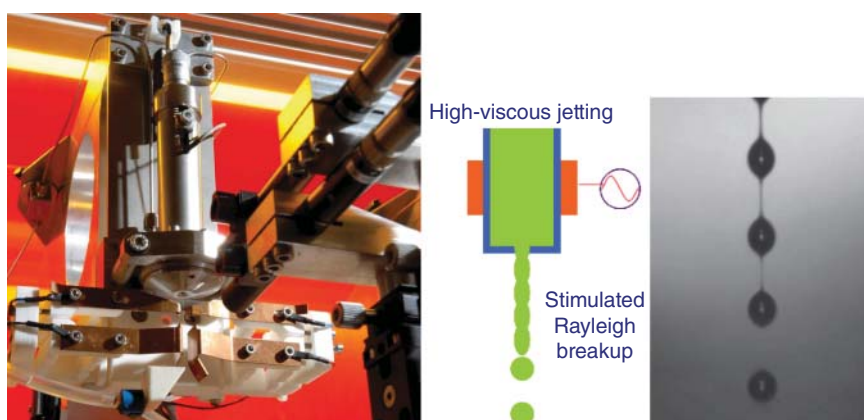


Figure 1.3 Image of a high-viscous inkjet system, schematic, and the resulting droplet shape.

3D metal microstructures, such as micro metal pillar arrays, helices, zigzag, and microbridges.

1.3.2 Laser-Induced Forward Transfer

LIFT is another digital printing technology [49]. LIFT differs from IJP especially in the manner of droplet formation. The source of the functional material is a donor sheet coated with a layer of ink or an evaporated or sputter-deposited solid film. This material is locally heated with a high-power, short-pulsed laser, released and transferred as a droplet onto an acceptor substrate located at some distance from the donor sheet. The release is either accomplished by direct heating of the functional material or by thermal or photochemical decomposition of a dynamic release layer located underneath the functional material. A schematic picture of the LIFT process is given in Figure 1.4.

A wide range of inks (from inkjet formulations to screen printing pastes) and even solid materials can be transferred using the LIFT process. The droplet formation and thereby printed spot size and spot definition are controlled by both the donor layer characteristics (composition and thickness) and by the laser parameters (fluence, wavelength, pulse length, and spot size). Optimizing laser pulse conditions is somewhat equivalent to waveform tuning in IJP [63, 64]. The optimization process is, therefore, a complex interplay between ink properties, donor layer thickness, and laser pulse parameters. Very high fluences can induce spray formation instead of well-defined jet formation or result in splashing droplets upon impact on the substrate (Figure 1.4). Donor layer thickness impacts the amount of transferred material, but changes made to this parameter usually require pulse parameter adjustment as well to remain optimal printing results. A homogenous and uniform layer thickness is a crucial prerequisite for reliable printing quality over larger areas.

Under optimized conditions, LIFT can produce well-defined narrow functional features with line widths in the order of a few micrometers [65]. Especially when high-viscous materials are transferred, high aspect ratio structures can be prepared, since there is hardly any spreading in these cases. In addition, certain

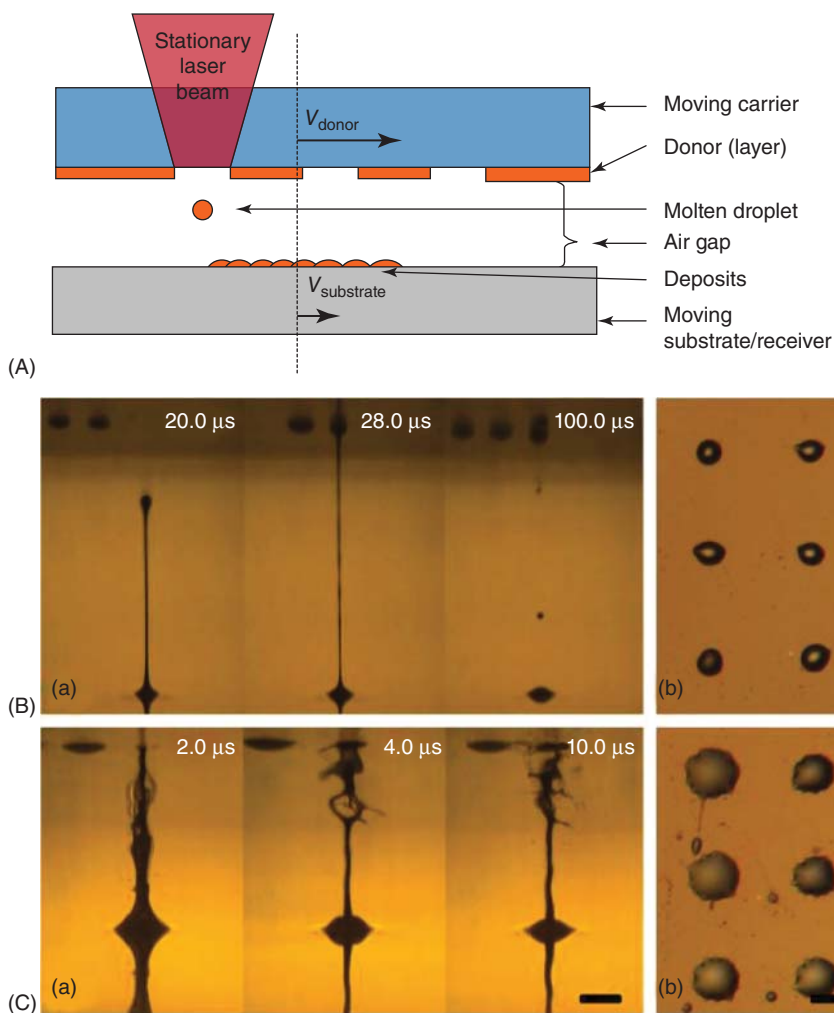


Figure 1.4 Principle of LIFT (A) and influence of laser fluence (100 (B) and 230 (C) mJ cm^{-2}) on jet formation and droplet size and definition of a silver nanoparticle ink [63]. Scale bars correspond to 50 μm . (Boutopoulos *et al.* (2014) [63]. Reproduced with permission of Springer.)

geometries such as very sharp turns with small radii can be difficult to prepare by IJP because they can easily break by unstable flow patterns aroused by the sharp kinks in the ink lines.

Although LIFT is a maturing technology, its potential for industrial application is still under development. Main challenges are the currently still limited processing speeds and process reliability, which is mainly due to the lack of reliable large-area coating mechanisms, which can supply donor substrates of extremely homogenous thickness.

If the laser is used in combination with a dynamic release layer, the donor material “only” undergoes a pressure wave lifting the material to the receiver

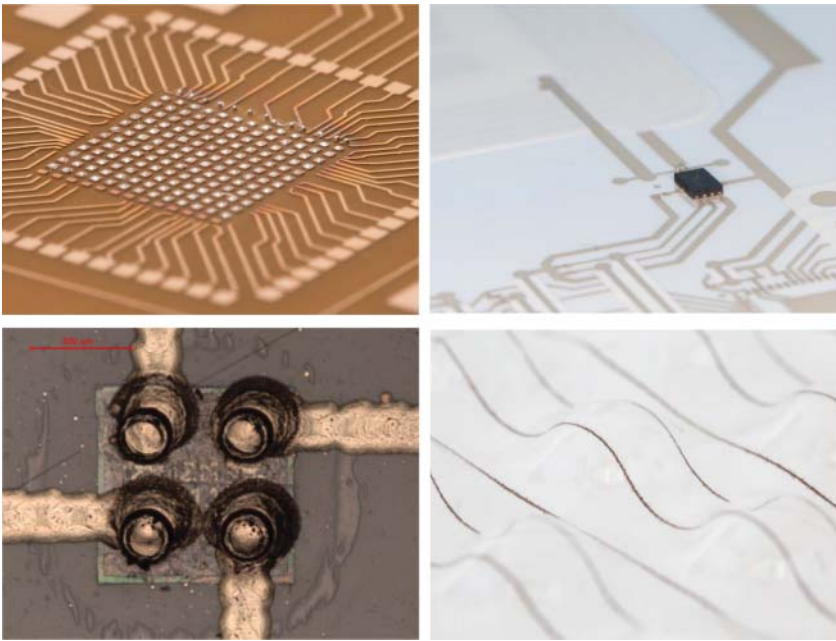


Figure 1.5 Examples of LIFT-printed interconnects and conformal lines on a curved surface.

substrate. This process is mainly adiabatic (room temperature) and does not harm the donor material. Hence, also living tissue cells and other temperature-sensitive (bio)materials can be printed in this way [66].

1.3.2.1 Toward 3D Printing

In addition to 2D features, the LIFT technology was also successfully applied to 3D printing. Examples include the transfer of solder pastes for 3D IC stacking, PCB bonding, and interconnect applications. An example is given in Figure 1.5 with 100 μm LIFT transferred features for PCB bonding and conformal printing on a curved surface, an achievement that is highly challenging for other printing technologies.

1.3.3 Contact Printing Technologies

Contact printing technologies make use of stencils or moulds with a predefined pattern to deposit ink onto the substrate and therefore offer less design and process compensation flexibility than, for example, IJP. On the other hand, these technologies can process higher viscosity and larger particle inks and are particularly well suited for industrial large volume production. In offset, gravure, and flexo printing, ink is transferred onto target substrates by means of printing rolls. These printing technologies involve a number of ink transfers from one to another carrier roll. Consequently, the amount of ink that is finally deposited on the target substrate is highly dependent on its relative affinities to the intermediate carrier roll materials. Printed layer thicknesses thus can vary considerably and can be

controlled by the selection of the roll materials' surface properties. As intrinsic roll-to-roll processes, offset, gravure, and flexo printing are all particularly well suited for continuous and high-throughput industrial production.

In offset printing, the surface of the printing roll is chemically patterned such that some surface sections attract the ink, while others repel it. The surface chemistry and the ink properties need to be well matched to create the required contrast in ink wettability. Although the entire roll surface is exposed to the ink, it will stick only to the parts where there are strong interactions and where it wets and spreads well, resulting in a thin film of ink on these spots. The contrast in surface wettability determines among others the printing properties such as layer thickness transfer, printing resolution, and feature definition. High printing speeds and rather good resolutions of down to $5\text{ }\mu\text{m}$ [67] can be achieved with offset printing, as long as the ink properties and printing parameters are in the correct range. Viscosities for ink formulations processed by offset printing are usually quite high, in the order of 40–100 Pa s.

In flexographic (or flexo) printing, the print pattern is present as a protruding relief on a printing roll, which is typically made out of a soft, rubber-like material (Figure 1.6). The ink is first transferred from a reservoir onto the printing roll by means of an anilox cylinder. This anilox cylinder consists of a metal roll with regularly engraved indentations (ink cells). Although these cells are present everywhere on the anilox surface, ink transfer occurs only to the elevated parts of the printing roll from where it is subsequently deposited onto the substrate. However, the pressures applied need to be kept rather low, to prevent excessive mechanical deformations of the protrusions, and consequently a decreased printing quality. Typical viscosities for flexo inks are rather low, between the values typical for IJP and offset printing (roughly 50–500 mPa s).

Microcontact printing (soft lithography) is somewhat similar to flexography and is the patterned transfer of a material onto a substrate by means of a relief silicone stamp [70]. Although in most cases self-assembled monolayers have been transferred using microcontact printing, it has also been applied directly for the patterned deposition of functional nanomaterials [71]. The striking feature of this approach is the impressive line width that can be achieved (below $1\text{ }\mu\text{m}$), which is

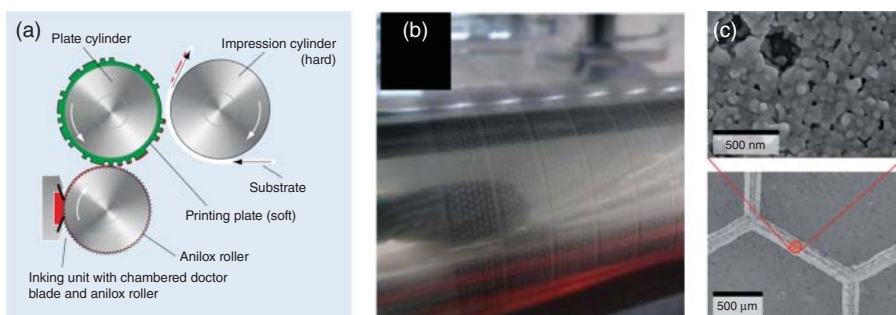


Figure 1.6 Schematic principle of flexo printing (a). (Kipphan (2001) [68]. Reproduced with permission of Springer.) Foil on roll with flexo printed silver ink (b) and microscopic images of the resulting conductive grid structure (c). (Yu *et al.* (2012) [69]. Reproduced with permission of Royal Society of Chemistry.)

unprecedented by other technologies. Upscaling to industrial production, however, has until now been a challenge.

In contrast to flexo printing, gravure printing makes use of a predefined pattern of indents engraved in a metal or plastic roll [15]. Ink transfer rollers are used to coat the gravure roll with the functional nanomaterial dispersion, and a squeegee or doctor blade knife is used to remove the excess of ink from the drum. The roller material needs to be rather rigid in order to allow proper ink removal from the roller surfaces. Ink viscosities need to be in the same range as for flexo printing. Advantages of the technology include high printing speeds and good printing resolutions. Due to the possibility of engraving different depths into the printing roller, printing of different layer thicknesses during one single printing run is easily possible, something which cannot be achieved with offset or flexo printing. A disadvantage of the technology is that large features need to be printed via a number of smaller cells, which are separated by cell walls. In particular for functional features and device functionality (for instance in the case of conductive tracks), these walls can form a serious shortcoming. Due to the high costs of the gravure roll, this technology is especially suited for industrial mass printing of large numbers of identical samples. At this moment, gravure printing is not yet a widely introduced manufacturing technology for functional nanomaterials but might become more attractive once printed electronic or biomedical devices are maturing.

A completely different approach is screen printing, in which the ink is pushed through a fine mesh of metal or polymer wires (Figure 1.7) [73]. Pattern definition is achieved by local closure of the mesh openings by means of a polymer film (emulsion). Structuring of this emulsion is typically carried out by selective removal of polymeric material using lithographic techniques. The transfer of the ink is achieved by a squeegee, which moves over the screen at a predefined speed and pressure, to squeeze the ink through the prepatterned mesh. As a consequence of this process, screen printing formulations are usually pastes with high viscosity (typically at least several pascal seconds [74]). Therefore, their solid loads can be very high, which, in combination with the thickness of the screens, results in feature heights unequaled by any other printing technology. The typical range is between 5 and 30 μm height, but extreme values of more than 100 μm have been shown for single-pass printing. Under laboratory conditions, line widths of 20 μm have been demonstrated [75], whereas for industrial processes the current limit is about 30–40 μm . This combination of line width and height results in the possibility to produce functional structures with large aspect ratios (around one), which can be very useful for a number of applications, for example, when high currents need to be transported through conductive lines of limited width/surface coverage. The most preferred screen printing pastes are generally shear thinning formulations, which display lower viscosities under shear, that is, when being squeezed through the mesh but solidify as soon as the shear is released, that is, after they have been deposited on the substrate [74]. Due to these rheologic characteristics, they allow the production of very well-defined structures, e.g., by limiting underflow, the unwanted deposition of paste underneath the covered areas of the screen. Although screen printing is by no means limited to the deposition of nanomaterials, it is widely used for this

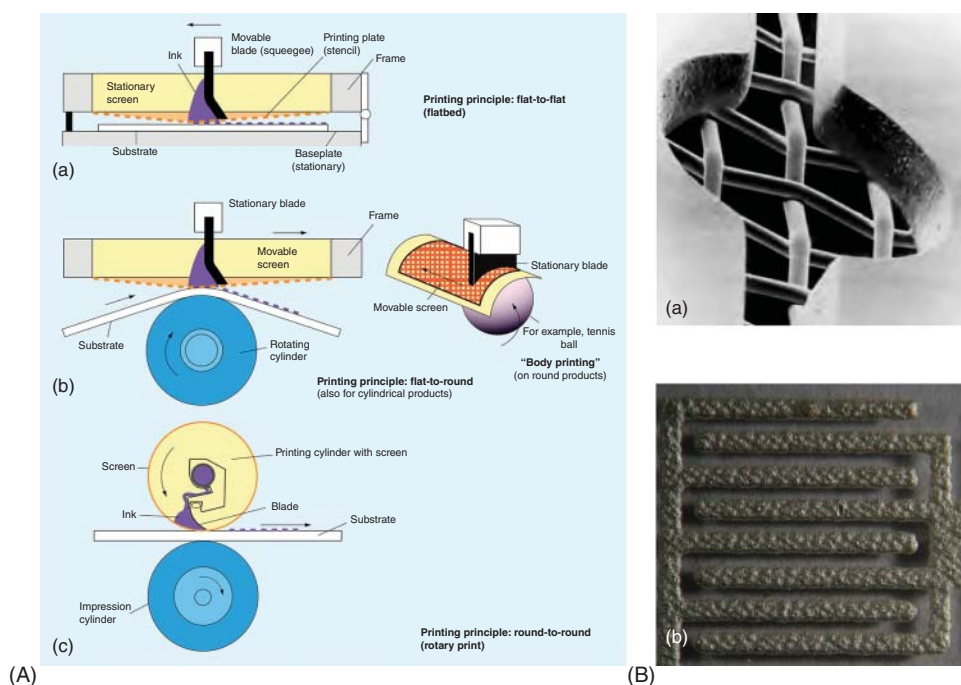


Figure 1.7 Schematic representation of various embodiments of screen printing (A). Electron microscopic image of a screen mesh partially covered with emulsion (B). (Kipphan (2001) [68]. Reproduced with permission of Springer.) Electrode pattern for a pressure sensor consisting of screen-printed graphene sheets and carbon nanotubes [72]. (Janczak (2014) <http://www.mdpi.com/1424-8220/14/9/17304/htm>. Used under CC BY 3.0 <http://creativecommons.org/licenses/by/3.0/>.)

class of materials, if the desired functionality dictates so. Since the technology is well established in industry, robust, highly reliable, and fast, screen printing has especially high prospects for applications in the mass manufacturing of functional devices based on functional nanomaterials. Roll-to-roll applicability when rotary screens instead of flatbed screens are used is an additional benefit, which allows continuous production at high speeds (up to 25 m min^{-1} [16, 76]).

The commercial success of printing as a feasible method for functional nanomaterials depends highly on the ability to be integrated in industrial mass production processes, which demand some critical conditions to be fulfilled. Printing technologies need to be superior in overall performance to the competing more traditional approaches, such as subtractive manufacturing. In order to achieve this, large amounts of products need to be produced at high fabrication speeds, which demands fast and large-area-compatible printing technologies. In this respect, roll-to-roll compatible technologies are especially interesting candidates to be considered, since they allow continuous processing to be applied [15, 16, 76–79]. At the same time, high process reliability with regard to process stability and consistent end-product performance are also crucial prerequisites. Under certain economic and technical boundary conditions,

sheet-to-sheet processing can outcompete roll-to-roll manufacturing, since the former approach can typically yield somewhat higher end-product qualities in terms of structural definition and resolution.

1.3.4 Photopolymerization

Vat photopolymerization (or SLA) is an optical manufacturing technology based on the selective and layer-by-layer photopolymerization of photocurable monomers. In the case of vat photopolymerization, the 3D product is built by light exposure of a film of resin through a baseplate and release of the exposed and cured part from the baseplate to allow new uncured resin to flow between the built part and the baseplate. This process is repeated numerous times to yield the final layer-by-layer manufactured part. In another embodiment, the exposure is from the top, and the product is step-by-step immersed in a vat of resin. These two embodiments are depicted in Figure 1.8. A major drawback of bottom-up vat photopolymerization is that the product needs to be carefully separated from the baseplate after each exposure to prevent damage. Novel solutions were developed to accelerate the separation without damaging the build. TNO developed a force feedback solution, which is based on the measurement of the force needed to separate the product from the plate and to use this information to accelerate the building process [80]. Carbon3D invented a process based on an inhibition layer between the baseplate and the part, preventing the adhesion of the part to the baseplate and thus accelerating the building process (even toward a continuous 3D print process) [81].

The technology allows for resolutions in the micrometer scale and below and for good dimensional stability. Challenges are in the field of productivity, part robustness, thermal stability, long-term stability, limited mechanical properties, outgassing, and biocompatibility.

The conventional systems were based on classical light sources, such as single beam laser, or digital light processors (switchable mirrors). The introduction of laser-array exposure in combination with advanced coating technologies has led to a new concept for photopolymerization. The system combines the

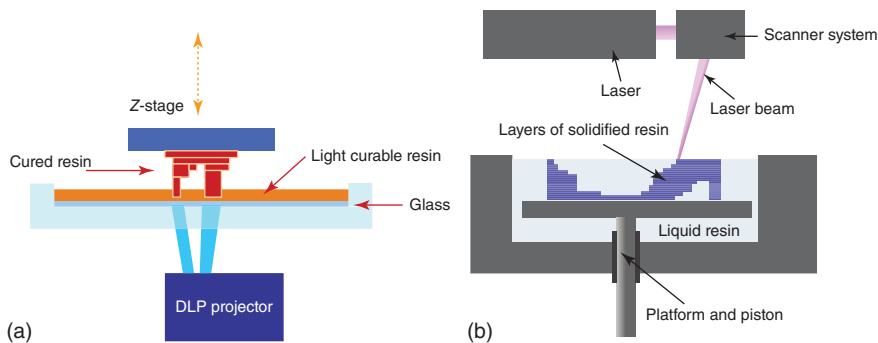


Figure 1.8 Two embodiments of photopolymerization: DLP in which a layer of resin is exposed by a pattern generated by a so-called digital light processor (a) and SLA where the pattern is created by a scanning laser beam (b).

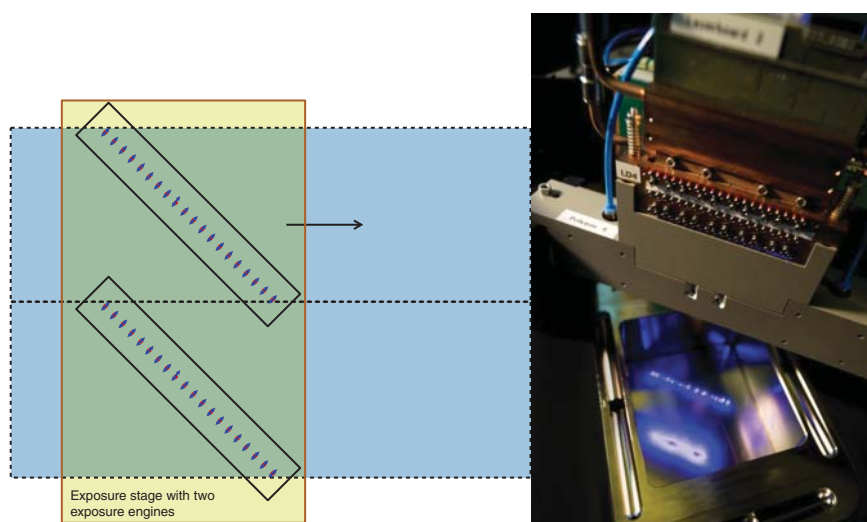


Figure 1.9 Sketch and picture of light engine based on multiple laser sources for high-resolution and large-area 3D printing [82].

advantages of high-resolution patterning ($10\text{--}20\text{ }\mu\text{m}$), fast single-pass exposure, large area exposure (the laser arrays are stitched to enable wide single-pass exposures), and coating of high-viscosity materials. The layout and a picture of the exposure engine are shown in Figure 1.9.

In general, four classes of vat photopolymerization materials are distinguished. The polymeric materials formed by photocuring of a (mainly organic) resin formulation are most commonly used. Typically, these materials consist of acrylate-based, acrylate–epoxy, or acrylate–oxetane hybrid formulations to meet application requirements. Challenges such as polymerization shrinkage and limited mechanical properties are addressed by organic–inorganic composites. In addition, 3D products can be made with composite resins, in which functional metal or ceramic (nano)particles are dispersed into an organic binder. The organic binder photopolymerizes and determines the part shape during the 3D build process. After 3D manufacturing, the binder material is thermally or chemically removed and the remainder is densified to reveal the final ceramic or metal part. A third class of materials is used for making moulds for metal or ceramic castings. Finally, photocurable materials are used as functional coatings applied on polymeric products. The main challenges in this field are adherence, layer consistency, and (mechanical and thermal) matching of materials.

Parts produced by photopolymerization are typically 100% dense but might have nonuniform properties and uncured resin fragments. Mechanical properties are inferior to nylon type materials used in thermal AM processes. To increase mechanical robustness (impact strength, modulus, etc.), photopolymers are nowadays reformulated and reengineered to adhere to the requirements imposed by high-tech applications, such as dental parts and high-tech parts.

Resins used in AM photopolymerization technologies have typically high covalent cross-link densities, leading to inferior mechanical properties (brittleness)

and mechanical deformations during the building process (because of internal stresses, warpage, and incomplete curing). Studies into improved mechanical properties target for improved polymer chemistry and additions.

1.3.5 Powder Bed Technology

Powder bed fusion (PBF) is a thermal process based on fusion or melting of particles to form 3D products. PBF is used to make metal and polymer parts. The process is based on the consecutive deposition of thin layers of powder via a roller or a coater process. A focused laser beam is used to locally melt or fuse the powder according to the predefined digital pattern. In this way, a digital image is transferred in a 3D part. Only the thermally affected material is fused into the 3D object, the unaffected material remains in the powder bed or is removed during the cleaning of the part. The key challenges of the PBF technology are part quality, production yield, dimensional stability, and material properties.

Because PBF is a thermal process, the material properties of the 3D printed part are determined by the temperature-time profile of each voxel inside the part. Voxels are typically heated multiple times, by cross-talk during exposure of adjacent and following tracks. In particular in the case of metal PBF, heat accumulation in the build product gives rise to thermally induced internal stresses and eventually to mechanical part deformation. Proper design of support structures to control the heat release from the part and laser scan strategies to better control the heating of the voxels have proven to improve the part quality significantly. However, further thermal control via optimized write strategies (with pulsed lasers and variable power settings) improved design strategies and in-line monitoring are required elements for obtaining part quality levels comparable to that obtained with conventional machining.

The particle characteristics, such as shape, size, and size distribution, determine to a great extent the mechanical properties and the surface quality of the printed part. Particle sizes typically range between 10 and 60 μm , depending on the material and application. Very small particles form clusters and prevent uniform recoating, while very large particles reduce the maximum layer packing density. The particle distribution determines the amount of absorbed laser light, the melting characteristics, the formation of pores and thereby the quality of the formed material, and the possible porosity of the final product. In most of the PBF technologies, a bimodal mixture of small and larger monodispersed powders is preferred for optimum printing performance, where the small particles fill the voids between the larger particles [83].

The lateral resolution is determined by the laser spot size and the thermally affected zone. The height resolution is also determined by the layer thickness of the deposited material. Layer thickness variation accumulates and impacts the following layers as well. This in turn may lead to incomplete sintering or melting with altered mechanical properties or porosity.

Binder jetting is a smart combination of selective deposition of a binder material in a powder bed. The binder locally binds the powder particles to reveal a green product. In a postprocessing step, heat treatment is used to release the binder and to further compact the 3D printed part.

1.4 Summary and Conclusions

The many different printing technologies currently available are a versatile toolbox for materials scientists and industry alike to deposit functional nanomaterials into well-defined patterns and structures both on flat surfaces and in three dimensions. They therefore form a highly valuable alternative to processing methods based on subtractive approaches or deposition from the vapor phase. The technical applications encompass biological and biomedical, electronic, catalytic, and a range of other functionalities. In order to allow an efficient printing process that best suits the envisioned functionality, the complex interplay of the nanomaterials with other ink ingredients, the printing technology, the substrate, and possible postdeposition treatments need to be well understood and carefully considered. Ink and paste formulations can be adjusted such that chemical and physical stability of the dispersed nanomaterials and a good processability are ensured. Depending on the specific requirements for the eventual materials or device properties, feature definition and resolution, layer thicknesses, and surface topologies, the choice for a particular printing technique can vary. Other important factors that determine which printing method suits a certain process best are its design flexibility, the mechanical stability of the used substrate (noncontact vs contact printing), and the intended production speed and volume. The recent progress in the field of functional nanomaterials processing to apply not only traditional printing techniques in two dimensions but also to include 3D printing has opened a wide and promising field for novel applications and devices.

References

- 1 Kamyshny, A. and Magdassi, S. (2014) Conductive nanomaterials for printed electronics. *Small*, **10** (17), 3515–3535.
- 2 Choi, H.W., Zhou, T., Singh, M., and Jabbour, G.E. (2015) Recent developments and directions in printed nanomaterials. *Nanoscale*, **7**, 3338–3355.
- 3 Habas, S.E., Platt, H.A.S., van Hest, M.F.A.M., and Ginley, D.S. (2010) Low-cost inorganic solar cells: From ink to printed device. *Chem. Rev.*, **110** (11), 6571–6594.
- 4 Khan, S., Lorenzelli, L., and Dahiya, R.S. (2015) Technologies for printing sensors and electronics over large flexible substrates: A review. *IEEE Sens. J.*, **15** (6), 3164–3185.
- 5 Mironov, V., Reis, N., and Derby, B. (2006) Bioprinting: A beginning. *Tissue Eng.*, **12** (4), 631–634.
- 6 O'Brien, C.M., Holmes, B., Faucett, S., and Zhang, L.G. (2015) Three-dimensional printing of nanomaterial scaffolds for complex tissue regeneration. *Tissue Eng., Part B*, **21** (1), 103–114.
- 7 Frazier, W.E. (2014) Metal additive manufacturing: A review. *J. Mater. Eng. Perform.*, **23** (6), 1917–1928.

- 8 Tekin, E., Smith, P.J., and Schubert, U.S. (2008) Inkjet printing as a deposition and patterning tool for polymers and inorganic particles. *Soft Matter*, **4**, 703–713.
- 9 Matsui, K., Yanagi, J., Shibata, M., Naka, S., Okada, H., Miyabayashi, T., and Inoue, T. (2007) Multi-color organic light emitting panels using self-aligned ink-jet printing technology. *Mol. Cryst. Liq. Cryst.*, **471** (1), 261–268.
- 10 Stewart, J.S., Lippert, T., Nagel, M., Nüesch, F., and Wokaun, A. (2012) Red-green-blue polymer light-emitting diode pixels printed by optimized laser-induced forward transfer. *Appl. Phys. Lett.*, **100**, 203303.
- 11 Coenen, M.J.J., Slaats, T.M.W.L., Eggenhuisen, T.M., and Groen, P. (2015) Inkjet printing the three organic functional layers of two-colored organic light emitting diodes. *Thin Solid Films*, **583**, 194–200.
- 12 Noh, Y.Y., Zhao, N., Caironi, M., and Sirringhaus, H. (2007) Downscaling of self-aligned, all-printed polymer thin-film transistors. *Nat. Nanotechnol.*, **2**, 784–789.
- 13 Lau, P.H., Takei, K., Wang, C., Ju, Y., Kim, J., Yu, Z., Takahashi, T., Cho, G., and Javey, A. (2013) Fully printed, high performance carbon nanotube thin-film transistors on flexible substrates. *Nano Lett.*, **13** (8), 3864–3869.
- 14 Liu, Y., Larsen-Olsen, T.T., Zhao, X., Andreasen, B., Søndergaard, R.R., Helgesen, M., Norrman, K., Jørgensen, M., Krebs, F.C., and Zhan, X. (2013) All polymer photovoltaics: From small inverted devices to large roll-to-roll coated and printed solar cells. *Sol. Energy Mater. Sol. Cells*, **112**, 157–162.
- 15 Jung, M., Kim, J., Koo, H., Lee, W., Subramanian, V., and Cho, G. (2014) Roll-to-roll gravure with nanomaterials for printing smart packaging. *J. Nanosci. Nanotechnol.*, **14** (2), 1303–1317.
- 16 Abbel, R., Teunissen, P., Rubingh, E., van Lammeren, T., Cauchois, R., Everaars, M., Valetton, J., van de Geijn, S., and Groen, P. (2014) Industrial-scale inkjet printed electronics manufacturing—production up-scaling from concept tools to a roll-to-roll pilot line. *Transl. Mater. Res.*, **1** (1), 015002.
- 17 Ru, C., Luo, J., Xie, S., and Sun, Y. (2014) A review of non-contact micro- and nano-printing technologies. *J. Micromech. Microeng.*, **24** (5), 053001.
- 18 Barbu, I., Ivan, M. G., Giesen, P., van de Moosdijk, M. and Meinders, E. R. (2009) *Advances in Maskless and Mask-based Optical Lithography on Plastic Flexible Substrates*. SPIE Proceedings 7520, Lithography Asia 2009, December 10, 2009.
- 19 Ivanova, O., Williams, C., and Campbell, T. (2013) Additive manufacturing (AM) and nanotechnology: Promises and challenges. *Rapid Prototyp. J.*, **19** (5), 353–364.
- 20 Zhu, W., Holmes, B., Glazer, R.I., and Zhang, L.G. (2016) 3D printed nanocomposite matrix for the study of breast cancer bone metastasis. *Nanomedicine*, **12** (1), 69–79.
- 21 Henmi, C., Nakamura, M., Nishiyama, Y., Yamaguchi, K., Mochizuki, S., Takiura, K. and Nakagawa, H. (2007) *Development of an Effective Three Dimensional Fabrication Technique Using Inkjet Technology for Tissue Model*

- Samples*. Proceedings of the 6th World Congress on Alternatives & Animal Use in the Life Sciences, August 21–25, 2007, Tokyo, Japan.
- 22 Konkoli, Z. and Wendin, G. (2013) *Toward Bio-inspired Information Processing with Networks of Nano-scale Switching Elements*. Proceedings of the NIP29 Digital Fabrication Conference, September 29–October 3, 2013, Seattle, United States.
 - 23 Hiller, J. and Lipson, H. (2010) Tunable digital material properties for 3D voxel printing. *Rap. Prototyp J.*, **16** (4), 241–247.
 - 24 Castro, N.J., O'Brien, J., and Zhang, L.G. (2015) Integrating biologically inspired nanomaterials and table-top stereolithography for 3D printed biomimetic osteochondral scaffolds. *Nanoscale*, **7**, 14010–14022.
 - 25 Gibson, I., Rosen, D.W., and Stucker, B. (2010) *Additive manufacturing technologies, rapid prototyping to direct digital manufacturing*, Springer. ISBN: 978-1-4419-1119-3 e-ISBN: 978-1-4419-1120-9.
 - 26 Cummins, G. and Desmulliez, M.P.Y. (2012) Inkjet printing of conductive materials: A review. *Circuit World*, **38** (4), 193–213.
 - 27 Rouhi, N., Jain, D., and Burke, P.J. (2011) High-performance semiconducting nanotube inks: Progress and prospects. *ACS Nano*, **5** (11), 8471–8487.
 - 28 Qi, Y., Jafferis, N.T., Lyons, K. Jr., Lee, C.M., Ahmad, H., and McAlpine, M.C. (2010) Piezoelectric ribbons printed onto rubber for flexible energy conversion. *Nano Lett.*, **10** (2), 524–528.
 - 29 Li, H.W., Muir, B.V.O., Fichet, G., and Huck, W.T.S. (2003) Nanocontact printing: A route to Sub-50-nm-scale chemical and biological patterning. *Langmuir*, **19** (6), 1963–1965.
 - 30 Withers, F., Yang, H., Britnell, L., Rooney, A.P., Lewis, E., Felten, A., Woods, C.R., Sanchez Romaguera, V., Georgiou, T., Eckmann, A., Kim, Y.J., Yeates, S.G., Haigh, S.J., Geim, A.K., Novoselov, K.S., and Casiraghi, C. (2014) Heterostructures produced from nanosheet-based inks. *Nano Lett.*, **14** (7), 3987–3992.
 - 31 Torrisi, F., Hasan, T., Wu, W., Sun, Z., Lombardo, A., Kulmala, T.S., Hsieh, G.W., Jung, S., Bonaccorso, F., Paul, P.J., Chu, D., and Ferrari, A.C. (2012) Inkjet-printed graphene electronics. *ACS Nano*, **6** (4), 2992–3006.
 - 32 Horn, A., Hiltl, S., Fery, A., and Böker, A. (2010) Ordering and printing virus arrays: A straightforward way to functionalize surfaces. *Small*, **6** (19), 2122–2125.
 - 33 Li, C., Hou, K., Yang, X., Qu, K., Lei, W., Zhang, X., Wang, B., and Sun, X.W. (2008) Enhanced field emission from ZnO nanotetrapods on a carbon nanofiber buffered Ag film by screen printing. *Appl. Phys. Lett.*, **93** (23), 233508.
 - 34 Grouchko, M., Kamysny, A., and Magdassi, S. (2009) Formation of air-stable copper–silver core–shell nanoparticles for inkjet printing. *J. Mater. Chem.*, **19**, 3057–3062.
 - 35 Frenzel, J., Joswig, J.O., Sarkar, P., Seifert, G., and Springborg, M. (2005) The effects of organisation, embedding and surfactants on the properties of cadmium chalcogenide (CdS, CdSe and CdS/CdSe) semiconductor nanoparticles. *Eur. J. Inorg. Chem.*, **2005** (18), 3585–3596.

- 36 Amstad, E., Textor, M., and Reimhult, E. (2011) Stabilization and functionalization of iron oxide nanoparticles for biomedical applications. *Nanoscale*, **3**, 2819–2843.
- 37 Dupont, J. and Meneghetti, M.R. (2013) On the stabilisation and surface properties of soluble transition-metal nanoparticles in non-functionalised imidazolium-based ionic liquids. *Curr. Opin. Colloid Interface Sci.*, **18** (1), 54–60.
- 38 Lara, P., Philippot, K., and Chaudret, B. (2013) Organometallic ruthenium nanoparticles: A comparative study of the influence of the stabilizer on their characteristics and reactivity. *ChemCatChem*, **5** (1), 28–45.
- 39 Yu, S.M., Laromaine, A., and Roig, A. (2014) Enhanced stability of superparamagnetic iron oxide nanoparticles in biological media using a pH adjusted-BSA adsorption protocol. *J. Nanopart. Res.*, **16** (7), 2484–2499.
- 40 Cherrington, R., Hughes, D.J., Senthilarasu, S., and Goodship, V. (2015) Inkjet-printed TiO₂ nanoparticles from aqueous solutions for dye-sensitized solar cells (DSSCs). *Energy Technol.*, **3** (8), 866–870.
- 41 Kettle, J., Lamminmäki, T., and Gane, P. (2010) A review of modified surfaces for high speed inkjet coating. *Surf. Coat. Technol.*, **204** (12–13), 2103–2109.
- 42 Derby, B. (2010) Inkjet printing of functional and structural materials: Fluid property requirements, feature stability, and resolution. *Annu. Rev. Mater. Res.*, **40**, 395–414.
- 43 Friederich, A., Binder, J.R., and Bauer, W. (2013) Rheological control of the coffee stain effect for inkjet printing of ceramics. *J. Am. Ceram. Soc.*, **96** (7), 2093–2099.
- 44 Majumder, M., Rendall, C.S., Eukel, J.A., Wang, J.Y.L., Behabtu, N., Pint, C.L., Liu, T.Y., Orbaek, A.W., Mirri, F., Nam, J., Barron, A.R., Hauge, R.H., Schmidt, H.K., and Pasquali, M. (2012) Overcoming the “coffee-stain” effect by compositional Marangoni-flow-assisted drop-drying. *J. Phys. Chem. B*, **116** (22), 6536–6542.
- 45 Abbel, R., Teunissen, P., Michels, J., and Groen, W.A. (2015) Narrow conductive structures with high aspect ratios through single-pass inkjet printing and evaporation-induced dewetting. *Adv. Eng. Mater.*, **17** (5), 615–619.
- 46 Grouchko, M., Kamyshny, A., Mihailescu, C.F., Anghel, D.F., and Magdassi, S. (2011) Conductive inks with a “built-in” mechanism that enables sintering at room temperature. *ACS Nano*, **5** (4), 3354–3359.
- 47 Lee, Y.I. and Choa, Y.H. (2012) Adhesion enhancement of ink-jet printed conductive copper patterns on a flexible substrate. *J. Mater. Chem.*, **22**, 12517–12522.
- 48 Agina, E.V., Sizov, A.S., Yablokov, M.Y., Borshchev, O.V., Bessonov, A.A., Kirikova, M.N., Bailey, M.J.A., and Ponomarenko, S.A. (2015) Polymer surface engineering for efficient printing of highly conductive metal nanoparticle inks. *ACS Appl. Mater. Interfaces*, **7** (22), 11755–11764.
- 49 Singh, S.C. and Zeng, H. (2012) Nanomaterials and nanopatterns based on laser processing: A brief review on current state of art. *Sci. Adv. Mater.*, **4** (3–4), 368–390.

- 50 Boissiere, C., Grosso, D., Chaumonnot, A., Nicole, L., and Sanchez, C. (2011) Aerosol route to functional nanostructured inorganic and hybrid porous materials. *Adv. Mater.*, **23** (5), 599–623.
- 51 Cibis, D. and Krüger, K. (2007) System analysis of a DoD print head for direct writing of conductive circuits. *Int. J. Appl. Ceram. Technol.*, **4** (5), 428–435.
- 52 Gan, H.Y., Shan, X., Eriksson, T., Lok, B.K., and Lam, Y.C. (2009) Reduction of droplet volume by controlling actuating waveforms in inkjet printing for micro-pattern formation. *J. Micromech. Microeng.*, **19** (5), 055010.
- 53 Kwon, K.S. and Lee, D.Y. (2013) Investigation of pulse voltage shape effects on electrohydrodynamic jets using a vision measurement technique. *J. Micromech. Microeng.*, **23** (6), 065018.
- 54 Morrison, N.F. and Harlen, O.G. (2010) Viscoelasticity in inkjet printing. *Rheol. Acta*, **49** (6), 619–632.
- 55 Ikegawa, M. and Azuma, H. (2004) Droplet behaviors on substrates in thin-film formation using ink-jet printing. *JSME Int J., Ser. B*, **47** (3), 490–496.
- 56 van Osch, T.H.J., Perelaer, J., de Laat, A.W.M., and Schubert, U.S. (2008) Inkjet printing of narrow conductive tracks on untreated polymeric substrates. *Adv. Mater.*, **20** (2), 343–345.
- 57 Soltman, D. and Subramanian, V. (2008) Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir*, **24** (5), 2224–2231.
- 58 Ishida, Y., Nakagawa, G., and Asano, T. (2007) Inkjet printing of nickel nano-sized particles for metal-induced crystallization of amorphous silicon. *Jpn. J. Appl. Phys.*, **46** (9B), 6437–6443.
- 59 Lee, M.W., Kang, D.K., Kim, N.Y., Kim, H.Y., James, S.C., and Yoon, S.S. (2012) A study of ejection modes for pulsed-DC electrohydrodynamic inkjet printing. *J. Aerosol Sci.*, **46** (4), 1–6.
- 60 Houben, R. (2012) Equipment for printing of high-viscous materials and molten metals, University of Twente Dissertation.
- 61 van Deventer, H., Houben, R., and Koldeweij, R. (2013) New atomization nozzle for spray drying. *Drying Technol.*, **31** (8), 891–897.
- 62 Ko, S.H., Chung, J., Hotz, N., Nam, K.H., and Grigoropoulos, C.P. (2010) Metal nanoparticle direct inkjet printing for low-temperature 3D micro metal structure fabrication. *J. Micromech. Microeng.*, **20** (12), 125010.
- 63 Boutopoulos, C., Kalpyris, I., Serpetzoglou, E., and Zergioti, I. (2014) Laser-induced forward transfer of silver nanoparticle ink: Time-resolved imaging of the jetting dynamics and correlation with the printing quality. *Microfluid. Nanofluid.*, **16** (3), 493–500.
- 64 Duocastella, M., Kim, H., Serra, P., and Piqué, A. (2012) Optimization of laser printing of nanoparticle suspensions for microelectronic applications. *Appl. Phys. A*, **106** (3), 471–478.
- 65 Piqué, A. and Kim, H. (2014) Laser-induced forward transfer of functional materials: Advances and future directions. *J. Laser Micro/Nanoeng.*, **9** (3), 192–197.

- 66 Koch, L., Kuhn, S., Sorg, H., Gruene, M., Schlie, S., Gaebel, R., Polchow, B., Reimers, K., Stoelting, S., Ma, N., Vogt, P.M., Steinhoff, G., and Chichkov, B. (2010) Laser printing of skin cells and human stem cells. *Tissue Eng., Part B*, **16** (5), 847–854.
- 67 Cho, H. (2014) Development of high-rate nano-scale offset printing technology for electric and bio applications. Northeastern University Dissertation.
- 68 Kipphan, H. (2001) *Handbook of Print Media, Technologies and Production Methods*, Springer, Heidelberg.
- 69 Yu, J.S., Kim, I., Kim, J.S., Jo, J., Larsen-Olsen, T.T., Søndergaard, R.R., Hösel, M., Angmo, D., Jørgensen, M., and Krebs, F.C. (2012) Silver front electrode grids for ITO-free all printed polymer solar cells with embedded and raised topographies, prepared by thermal imprint, flexographic and inkjet roll-to-roll processes. *Nanoscale*, **4** (19), 6032–6040.
- 70 Carlson, A., Bowen, A.M., Huang, Y., Nuzzo, R.G., and Rogers, J.A. (2012) Transfer printing techniques for materials assembly and micro/nanodevice fabrication. *Adv. Mater.*, **24** (39), 5284–5318.
- 71 Kang, H.W., Leem, J., Ko, S.H., Yoon, S.Y., and Sung, H.J. (2013) Vacuum-assisted microcontact printing (μ CP) for aligned patterning of nano and biochemical materials. *J. Mater. Chem. C*, **1**, 268–274.
- 72 Janczak, D., Słoma, M., Wróblewski, G., Młodziak, A., and Jakubowska, M. (2014) Screen-printed resistive pressure sensors containing graphene nanoplatelets and carbon nanotubes. *Sensors*, **14** (9), 17304–17312.
- 73 Li, M., Li, Y.T., Li, D.W., and Long, Y.T. (2012) Recent developments and applications of screen-printed electrodes in environmental assays—A review. *Anal. Chim. Acta*, **734**, 31–44.
- 74 Lin, H.W., Chang, C.P., Hwu, W.H., and Ger, M.D. (2008) The rheological behaviors of screen-printing pastes. *J. Mater. Process. Technol.*, **197** (1–3), 284–291.
- 75 Hyun, W.J., Lim, S., Ahn, B.Y., Lewis, J.A., Frisbie, C.D., and Francis, L.F. (2015) Screen printing of highly loaded silver inks on plastic substrates using silicon stencils. *ACS Appl. Mater. Interfaces*, **7** (23), 12619–12624.
- 76 Krebs, F.C. (2009) Polymer solar cell modules prepared using roll-to-roll methods: Knife-over-edge coating, slot-die coating and screen printing. *Sol. Energy Mater. Sol. Cells*, **93** (4), 465–475.
- 77 Dam, H.F., Andersen, T.R., Madsen, M.V., Mortensen, T.K., Pedersen, M.F., Nielsen, U., and Krebs, F.C. (2015) Roll and roll-to-roll process scaling through development of a compact flexo unit for printing of back electrodes. *Sol. Energy Mater. Sol. Cells*, **140** (9), 187–192.
- 78 Angmo, D., Andersen, T.R., Bentzen, J.J., Helgesen, M., Søndergaard, R.R., Jørgensen, M., Carlé, J.E., Bundgaard, E., and Krebs, F.C. (2015) Roll-to-roll printed silver nanowire semitransparent electrodes for fully ambient solution-processed tandem polymer solar cells. *Adv. Funct. Mater.*, **25** (28), 4539–4547.

- 79 Noh, J., Yeom, D., Lim, C., Cha, H., Han, J., Kim, J., Park, Y., Subramanian, V., and Cho, G. (2010) Scalability of roll-to-roll gravure-printed electrodes on plastic foils. *IEEE Trans. Electron. Packag. Manuf.*, **33** (4), 275–283.
- 80 Maalderink, H.H., Michels, J.J. and Boot, R.J.J. (2010) System and method for producing a tangible object. European patent EP2043845.
- 81 Tumbleston, J.R., Shirvanyants, D., Ermoshkin, N., Januszewicz, R., Johnson, A.R., Kelly, D., Chen, K., Pinschmidt, R., Rolland, J.P., Ermoshkin, A., Samulski, E.T., and DeSimone, J.M. (2015) Continuous liquid interface production of 3D objects. *Science*, **347** (6228), 1349–1352.
- 82 Jamar, J.H.T., Maalderink, H.H., Meinders, E.R., Giesen, P.T.M., van Zwet, E.J. and Starman, H.J.A.J. (2015) Exposure head, exposure apparatus and method of operating an exposure head. WIPO Patent Application WO/2015/160252.
- 83 <http://www.insidemetaladditivemanufacturing.com/blog/the-role-of-super-powders-in-slm> (26 January 2016).

2

Inkjet Printing of Functional Materials and Post-Processing

Ingo Reinhold

2.1 Introduction

The pioneering work of Hewlett Packard and Canon for the development of inkjet printers during the 1980s made inkjet affordable and part of every home and office all over the world. With further development into more industrial-type applications, inkjet grew into an indispensable tool for replacing existing analog techniques and enabled completely new production technologies. Especially piezo-based drop-on-demand (DoD) systems were proven to dispense a variety of low-viscosity functional fluids and provided the inherent advantages of digital inkjet technology (digital, noncontact, additive, and scalable), which allowed for the implementation of *digital fabrication* processes.

Early commercial industrial applications of inkjet were in the wide- to grand-format printing of graphics, posters, and banners, which was followed by some applications such as packaging all the way into commercial print. Starting from these purely graphical applications, digital printing of flooring and décor was pursued and is now one of the biggest commercial successes. In order to comply with throughput expectations for these markets, machines comprising more than 150 000 nozzles are being developed and applied. In the case of ceramic tiles, screen printing, which was the *de facto* standard for production, was almost fully replaced by digital within only a few years, because benefits such as the absence of physical masks, random patterns, and variable run lengths, as well as manufacturing of surface topography, proved to be superior.

Since inkjet has started to be used more as a *material jet* than solely as a graphical tool, applications and development toward a whole new level arise, where *printing beyond color* renders possible. In these emerging applications, often the reduction of material waste is addressed, where spin coating or subtractive processes involving precious and expensive fluids become 80% more efficient through the application of the fluid at the point of interest only. Piezo-based inkjet technologies are of high importance here. Their capability of jetting a variety of different base solvents (aqueous, solvent, oil, and UV) in conjunction with the possibility to jet higher viscosity fluids (≤ 20 cP inside the channel) allowed for the dispensing of functional materials for the manufacturing of printed electronics, displays, solar cells, smart packaging, and pharmaceuticals.

In contrast to the number of publications utilizing inkjet technology for the generation of a multi-layers in an application, the commercial application lags somewhat behind, as the *lab-to-fab* transition is relatively complicated. Big challenges are found in the wetting properties of the used inks on multimaterial substrates, drying phenomena in thin liquid films, and the removal of ink additives for the maximization of the functionality.

2.2 Industrial Inkjet

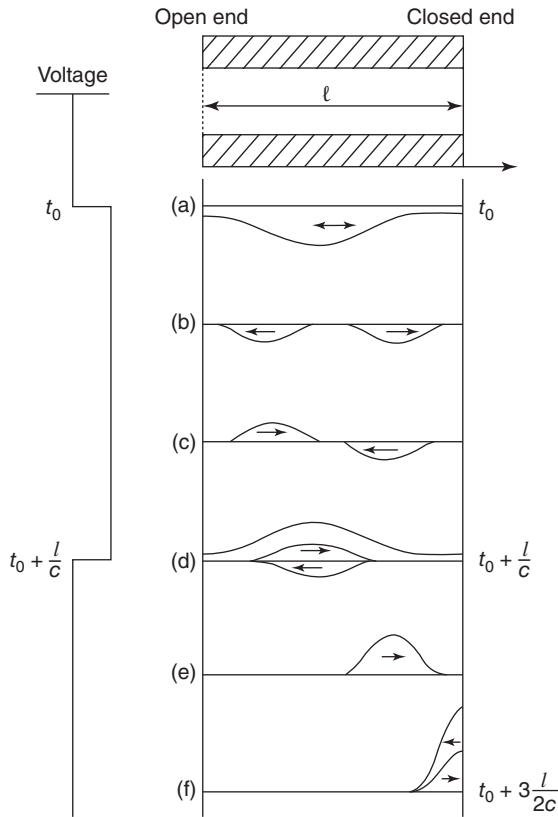
In industrial piezo-based inkjet systems, an acoustic phenomenon is exploited in order to generate jets from an orifice at high frequencies. *Acoustic firing* refers to the utilization of the superposition of pressure waves in acoustic resonators for the production of short, high-pressure pulses at a nozzle, leading to the deflection of a meniscus and the generation of a droplet. In these systems, the properties of polarized piezoceramics are employed, where an applied electric potential gradient may be used for the acceleration of the surface in different directions and thereby change the cross-sectional area of a microchannel. With creating the initial potential gradient expanding the channel, a wave with a negative magnitude with respect to atmospheric pressure is generated. Due to the micrometer dimensions of the channel being small compared to the acoustic wavelength, this wave is essentially one dimensional and moves with half the magnitude toward either end of the channel (cf. Figure 2.1). There the wave experiences a step in acoustic impedance, yielding a phase shift of the reflected wave at the open fluidic end (zero pressure boundary condition) and noninverting reflection at the closed boundary (zero velocity boundary condition). One acoustic period after the initial deformation of the channel, that is, the time needed for the wave to travel a whole length of the channel at the compliance-corrected speed of wave propagation c , the two waves superimpose and create a momentary zero pressure [1]. In this instant, the potential gradient is removed externally and the piezoceramic creates an acceleration in the opposite direction, which superimposes a positive pressure wave. The sum of the inverted pressure wave and half the magnitude of the superimposed wave now travel jointly toward the nozzle and allow for the generation of a liquid jet, which will break off as a result of the Plateau–Rayleigh instability.

For industrial production throughput, reliability and precision are the decisive characteristics. In order to achieve these performance criteria, the printheads as well as the ink need to be matched. For an initial assessment of a fluid, the Ohnesorge number is often utilized, which relates the viscous forces to inertial and surface tension force [3].

$$\text{Oh} = \frac{\mu}{\sqrt{\rho\sigma l}} \quad (2.1)$$

where μ , ρ , σ , and l are the fluid's viscosity, density, surface tension, and a characteristic length, respectively. Values for jettable fluids are typically given in the range of 0.1–1, where the interplay between viscosity and surface tension support the formation and acceleration of a droplet [4, 5]. This results in the

Figure 2.1 Acoustic principle of droplet formation in an end-shooter type printhead with a manifold connection (open end) and a nozzle plate (closed end) [l length of the cavity, c compliance-correct speed of wave propagation in the channel]. Bogoy and Talke (1984) [2]. Reproduced with permission of IBM.



typical operating range of industrial inkjet printheads, where the viscosity of the fluid ranges from 5 to 25 mPa s and the surface tension is in the order of 25–35 mN m⁻¹. The lower limit of the viscosity range relates to the efficiency of viscous dissipation of the residual energy in the channel to enable high droplet repetition rates, whereas the upper limit is defined by the pumping power or strength of the printhead. The latter furthermore defines the upper limit for the surface tension, as the force opposing meniscus deformation would exceed the force generated by the pressure wave and no droplet could be expelled. The lower surface tension limit further relates to reliability issues resulting from excessive meniscus ringing or wetting of the fluid onto the nozzle plate.

The process is, however, extremely dynamic (typical piezoactuation frequencies of 200 kHz, shear rate inside the nozzle around 500 000 s⁻¹), and standard measurements provide only limited insights into the performance of a fluid in conjunction with an inkjet printhead. Especially the rheological measurements, typically using a simple stress state applied to a fluid sample in plate-cone or rotating cylinder rheometers, have only limited relation with the stress of squeeze flow inside the channel, the high shear in the nozzle, or the extensional stress experienced during droplet formation. A lot of work, therefore, focused on extending the frequency range as well as sensitivity of rheological tools and simulation models to accommodate the effects of viscoelasticity and dynamic surface tension

[6–11]. Especially the viscoelastic properties play an important role [12] as they enable the optimization of the ink to provide satellite-free droplets.

In functional applications, the optimization of inkjet inks is often performed with respect to the performance on the final substrate and rarely to the printhead. The challenge in these systems is to find a balance between functionality and reliable operation in the printhead, which are closely linked [13]. In order to compensate some of the fluid's shortcomings, complex driving waveforms applied to the PZT actuators are considered. Using these, droplet formation can be affected to not solely rely on the Rayleigh-type droplet formation, but trigger droplet detachment and satellite suppression. Furthermore, the time for complete cancellation of residual waves in the actuator may be reduced to enable higher droplet ejection rates.

Recently, different printhead technologies were introduced that employ ink flow inside the printhead to extend the mean time between maintenance [14–16]. This is mainly attributed to the possibility to remove ingested air, which would otherwise result in a nozzle outage due to the breakdown of the acoustics inside the channel. In addition, reliability improves due to the constant circulation of ink, allowing for the processing of quickly settling dispersions as well as improved temperature consistency across the actuator due to the cooling effect and heat exchange of the ink with actuator material and electronic components. While these benefits are essential for the introduction of inkjet technology into industrial applications, the testing procedures required during ink development are somewhat more stringent. The fluid formulations need to be able to withstand continuous shearing at different shear rates as they pass through the pumps, tubing, and filters into the printhead and back into the reservoir, where effects such as heterocoagulation in converging flows [17] and insufficient attractive forces between particles and dispersant may be reasons for ink destabilization.

2.3 Postprocessing of Metal-Based Inks for Conductive Applications

The creation of conductive features from inkjet-printed, nonconducting deposits typically involves different paths depending on the ink technology used. These approaches eventually result in the generation of nanoparticles or clusters, which subsequently need to merge into a cohesive structure with a strongly reduced number of electron-scattering centers in order to provide a low intrinsic resistance.

Inkjet inks for conductive applications are commonly divided into two different classes: (i) precursor inks, such as metal salts or metal organics compounds (MODs) dissolved in suitable solvents or (ii) nanoparticle inks. In the former case, the metal is attached to an organic backbone or present in its oxidized form. Hence, it needs to be reduced to make it available for the formation of nanoparticles and eventually conductive films. In the latter case of nanoparticles, where the metal is present in its elemental form, anchoring groups such as low-molecular-weight carboxyl, amines, or thiols as well as

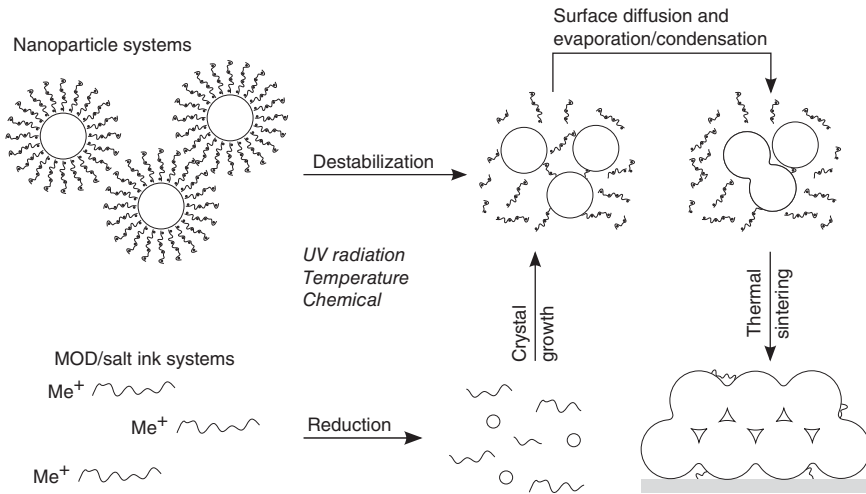


Figure 2.2 Schematic overview of the different routes to metallic deposits derived from inkjet-processable inks.

amphiphilic polymers, which are used to stabilize the particles in solution, need to be removed to allow for metal–metal contact between the particles. While occasionally chemical destabilization techniques are exploited [18, 19] and sintering is achieved using the intrinsic driving forces of the nanoparticles, most often the application of thermal energy is utilized to enable the redistribution of matter and, hence, sintering of the deposits [20–30].

After the successful creation of nanoparticles and their initial contact (cf. Figure 2.2), the constriction resistance of a neck between two touching particles R_{cr} is given as

$$R_{cr} = \frac{\rho_{el}}{2r_n} \quad (2.2)$$

where ρ_{el} corresponds to the intrinsic resistivity of the particle material and r_n is the radius of the neck formed between the particles [31]. The inverse relation to the radius of the formed neck between two particles clearly highlights the importance of the neck growth, as a neck in the nanometer range would still contribute an ohmic resistance in the single digit range. A second strong contribution to the resistance of nanosized films comes from grain boundary scattering [32, 33]. While multiple percolation paths will be created during the sintering process, the minimization of electric resistance by increased neck, particle, and grain size through sintering is essential.

In printed functional applications, the desire is to apply the functional structures to low-cost substrates with glass transition temperatures often considerably lower than 200 °C. At such low temperatures and processing times suitable for industrial processes, final stage sintering and hence the anticipated functional properties may not be achieved. As a result, much research concentrated on identifying processes that selectively heat the functional deposit irrespective of the underlying substrate in order to trigger sufficient material flow. The approaches

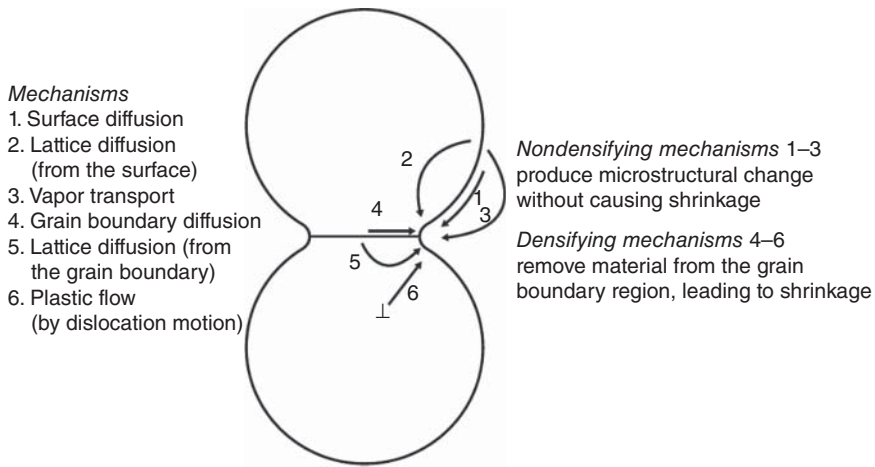


Figure 2.3 Sintering mechanisms schematically depicted for the simplified case of two touching particles. Fang and Wang (2010) [49]. Reproduced with permission of Elsevier.

taken include plasma [20, 34–36], microwave, and electrical [37–41] as well as photonic sintering [41–48].

In the following, the driving forces for sintering of nanoparticles are discussed, as these provide the basis for the understanding of the resulting characteristics of the materials. In addition, some of the alternative approaches are introduced and discussed with respect to the specific strengths as well as challenges in implementation. Furthermore, the influence of drying of the printed ink as a major limiting factor in productivity as well as the influence of the substrate on sintering performance is discussed.

2.3.1 Mechanisms in Solid-State Sintering

Sintering of particulate materials is generally dependent on the composition, the particle size, heat rate, sintering temperature, sintering time, liquid phase formation, and so on [49]. Sintering in general is driven by the tendency to reduce the overall system energy by the motion of atoms and vacancies. This mass transport is typically accomplished by interfacial (surface diffusion, grain boundary diffusion, and condensation–evaporation) or by volume diffusion processes (viscous flow and dislocation climb), which are schematically depicted in Figure 2.3.

The involved material transport mechanisms typically follow an Arrhenius-type behavior, and the respective diffusion coefficient D obeys the general form

$$D = D_0 \exp \left(-\frac{Q}{RT} \right) \quad (2.3)$$

where D_0 is a scaling factor, Q the activation energy, R the universal gas constant, and T is the absolute temperature. Hence, the diffusivity changes mainly with the activation energy Q , which reflects the energy necessary for moving atoms according to the respective diffusion mechanism, and the temperature T , which modulates the amount of free atoms and vacancies.

Interfacial transport mechanisms such as surface diffusion and evaporation–condensation are the predominant mechanisms in low-temperature sintering and during the initial stage sintering ($\leq 70\%$ of the theoretical density). Three different steps are commonly needed to move atoms along a surface: (i) breaking of the bond to the surface, (ii) random motion of the atom on the surface, and (iii) reattachment of the atom at a vacancy site. The surface tension γ , which provides excess energy resulting from broken bonds and/or defects at the free surface of the solid particles, is the primary thermodynamic driving force. It is, therefore, related to the internal bond structure of the materials, assigning for instance higher surface energy to higher melting point materials. Surface tension in conjunction with a curvature (radii $R_{1,2}$) creates a capillary stress σ that forces surfaces to move during sintering, where mass flow from convex (vacancy deficient) to concave (vacancy excess) surfaces is triggered in order to minimize the surface energy.

$$\sigma = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.4)$$

The relationship clearly shows the inverse relationship between stress and particle size, which results in a reduction of the activation energy and, therefore, an increased surface diffusivity. The growth of the neck between two touching particles will continue until the neck reaches an equilibrium, which is determined by the surface energy (consumption of defective surface as well as surface area), the dihedral angle, and grain boundary energy.

From a vacancy point of view, the driving force can be even higher, as the linearization of the Gibbs–Thomson equation, which describes the magnitude of the driving force for mass transport as a function of surface curvature, is no longer valid for nanometer-sized particles and hence scales exponentially as the particle size decreases [49]. In the case of nanoparticles, surface diffusion can indirectly contribute to densification as it will trigger coarsening, or *Ostwald ripening*, and therefore allow for grain growth by growth of larger particles at the expense of smaller particles. Furthermore, surface melting of the nanometer-sized particles [50] may allow for processes such as particle rotation, sliding, and viscous flow at lower temperatures leading to higher diffusivity and enhanced grain growth.

Grain-boundary energies, which arise from misalignment of the lattices of neighboring grains, represent a defective interface and, therefore, a possibility for energy reduction by transport of vacancies. Grain boundary energy–driven sintering is one of the dominant processes for densification especially in the intermediate stage of sintering (70–90% of the theoretical density), as the activation energy is intermediate to the values for surface and bulk diffusion mechanisms.

At elevated temperatures and longer sintering times, bulk transport mechanisms may be triggered, which allow for a particle-size and composition-dependent motion of atoms from the inside toward the surface of the particle or the growing neck, where vacancies are annihilated. The involved processes are volume diffusion, plastic, and viscous flow and dislocation climb. While bulk transport is often associated with densification, not all processes allow for an approach of the centers of neighboring spheres. For example, does volume

diffusion adhesion transport atoms from the surface through the lattice to the neck surface, which equals the result of a nondensifying interfacial transport. Dislocation flow may also be present during the initial stage of sintering and when using small particles. It, however, quickly loses importance because dislocations are consumed as the neck grows, and the shear stress falls below the critical value for dislocation flow.

Due to the temperature limitations of the substrates used in combination with printed materials, bulk transport mechanisms are seldom triggered when applying conventional thermal sintering. However, novel techniques to selectively couple energy into particles generate high temperatures for short periods of time [51, 52] and hence may trigger increased densification based on bulk material transport.

2.3.2 Influence of Drying and Wet Sintering

In functional inkjet printing, the amount of functional material by volume is often much lower than 10% due to the adaptation of viscosity to omit overly strong dampening of the acoustics inside the printhead. Hence, more than 90 vol% of solvent have to be depleted from the substrate before sintering of nanoparticles can be initiated. This drying step is often time limiting as evaporation from the nonporous substrate may be limited by the allowable temperature rise – without explosive evaporation of the solvent – as well as the allowable temperature for the substrate.

The presence of the surrounding liquid often complicates the formation of well-defined structures due to instabilities related to the surface energy of the substrate and the surface tension of the liquid. Soltman *et al.* [53–55] showed the influences and provided insights into preflight checks for print patterns without the influence of actual evaporation of the solvent.

The dynamics of evaporation strongly influence the deposition of the functional constituents and the realization of the final functionality mostly on nonabsorbing substrates. So can the differential evaporation rate due to the varying radius of curvature of the deposit's surface and the used solvents generate a preferential deposition of material either on a pinned contact line (*coffee stain*) or in the center [56–58]. Counteracting measures can be taken in the ink formulation using binary mixtures of solvents [57] or the addition of fluorosurfactants [59] that initiate Marangoni flows to counteract the gradient-driven outward flow of constituents. Furthermore, different results may be generated by an unpinned contact line, where the sequential evaporation of ink constituents results in the contraction of an inkjet-printed line and the generation of high-aspect-ratio functional deposits [60].

The drying step is also critical with respect to sintering, as the formation of agglomerates dictates the sintering characteristics with respect to achievable densities. The number of particles surrounding the pores, the so-called coordination number of a pore, alongside with the dihedral angle defines whether a pore will shrink or grow during the process of sintering. When considering nanoparticle systems, typically coordination numbers are larger than the critical value and densification is prevented. Hence, suppression of large agglomerates

during drying should be of benefit when dense and highly conductive features are anticipated [49].

2.3.3 Thermal Sintering

The application of thermal energy is until now the most common form for sintering nanoparticles or MOD composites. While the melting point depression in nanosized metal crystals and the mechanisms available during initial stage sintering can generate reasonably conductive structures, the major challenge is typically to remove the capping polymers from the surface of the nanoparticles, break down the polymer backbones, or reduce the metals to their elemental state. For metal salts, a typical approach is to synthesize them into a suitable complex, which shows a clear reduction in the decomposition temperature [61]. For nanoparticles, different systems of capping agents, which alter the binding energy to the nanoparticle surface, have been utilized.

While often thermal decomposition of the additives used in ink formulations requires temperatures higher than 200 °C, conductive structures are often found way below this temperature. The reason for this is the detachment between the metallic constituents and the stabilizers, which enables sintering [62]. Greer and Street [63] pointed out that heating above the solvent boiling point initiates polymer flow, allowing interparticle contact and formation of metallic contacts at temperatures as low as 100 °C, whereas densification was pronounced at higher temperatures. This is substantiated by the findings of Chou *et al.* [64] who showed that the capping polymer (poly(vinylpyrrolidone)) is detached from the surface of the nanoparticles at a temperature as low as 70 °C. The remainder of the stabilizer, however, persists in the matrix of conductive particles and dictates the pore sizes by changing the dihedral angle and therefore lowers the effective conductivity of the structure. A more desired side effect of the remaining stabilizers is often found in the improved adhesion to the underlying substrate in circumstances, where the interaction of the metal clusters with the substrate is particularly strong, as in the case of polymeric foils (C. Schauer and A. Rösch (2015) Personal Conversation.).

The major challenge for the industrial adoption of the technique is the time duration of sintering. Depending on the type of application of the heat (hot plate and convection ovens), results vary but typically are in the tens of minutes for consistent results. Given the ambition of having roll to roll processing, this typically contradicts the machine size expectations, as even typical printing speeds of 0.1–0.2 ms⁻¹ require a sintering length of 6–12 m assuming a sintering time of 10 min. Creative concepts to shorten the overall length of the ovens, however, make thermal annealing a reliable sintering choice, especially when sintering stacks of different materials.

2.3.4 Chemical Sintering

Purely chemical approaches were also considered to enable substrate-independent sintering. The chemical effect, however, does not directly relate to sintering of the metal particles released from the ink, but more to the release itself. Hence, the chemical sintering agents trigger removal or destabilization

of the capping molecules in nanoparticle systems or the reduction of the metal cation in the case of MOD-based inks.

In nanoparticle systems, the typical process is the reduction of the bond of the dispersant to the surface of the nanoparticle, where the stability of the capping agent–particle interaction is strongly dependent on the chemistry used. Hence, different approaches were presented in the literature. These include dissolving capping dodecylamine using alcohols [65], neutralization of charges using cationic polymers on polyacrylic acid–stabilized nanoparticles [27], sequential deposition of ink and sintering agents of NaCl and MgCl_2 solutions [19], or the exposure to hydrochloric acid vapor [66, 67]. An intriguing approach was demonstrated by Grouchko *et al.* [29], where the sintering agent was incorporated into the ink and destabilization was triggered during drying. Here, the accompanying increase in the concentration of chloride ions was responsible for the destabilization of the polyacrylic acid–stabilized nanoparticles. One challenge indicated by the authors was the rather low packing density of the particles, which arose from the spontaneous agglomeration of the particles in the late stages of drying.

When using complexes or metal salt inks, mostly reactive inkjet printing is considered for the reduction of the contained metal cation. In this method, the subsequent deposition of two different reactants is necessary, which typically complicates the machine concept and results in by-products that need to be removed from the created functional layer by evaporation or rinsing steps. A secondary challenge originates from the following phenomena: whether the release of the zero valent metal is accomplished in a solution, whether cluster formation and reorganization can take place before the solvent is removed by evaporation, or whether intermediate drying is necessary to ensure the geometrical integrity of the track.

For further details on sintering mechanisms based on chemical interaction, the interested reader may refer to Chapter 7.

2.3.5 Plasma Sintering

The interaction of accelerated, charged species with a surface is very important in materials processing [68] and was shown to be applicable to the initiation of sintering in printed deposits. Plasmas are a collection of charged bodies, which are on average electrically neutral. In the low-pressure, weakly ionized case, plasmas are often driven electrically, whereby electrons are accelerated and, by the inelastic interaction with neutrals, transfer energy to create positive ions, free radicals, and further electrons. Electron impact is the major mechanism to create positive ions but other effects such as photoionization, secondary emission, and electron attachment producing negative ions also play important roles in plasma processing.

Early studies utilized low-pressure plasma chambers as they are known from plasma cleaning. Gases typically used in these applications include argon and oxygen, which produce inert or highly oxidizing plasmas, respectively. For silver, whose oxides are degenerate semiconductors, oxidation is typically not detrimental. Materials such as copper, however, may suffer from the generation of their oxidized species and lose electrical conductivity. Argon was chosen for a variety

of experiments due to its nonreactive nature [35, 36, 69, 70]. The experiments clearly showed the applicability of the process, resulting in effective conductivities of 10–20% compared to bulk silver. Hence, the impact of the created ions and the stopping power show a clear projectile–target interaction. This leads to chain scission in the capping polymer shell or the polymer backbone and induced material transport between particles. The mechanisms involved could include condensation–evaporation, energy transfer through physical bombardment as well as slight temperature increase below the glass transition temperature of typically used polymeric substrates most likely due to the interaction of the electromagnetic fields from the plasma system with the substrate holder.

While densification of up to 40% compared to the green state was observed, an increase in the conductance in multilayer experiments was absent. The reason was found to originate from the creation of a dense and highly conductive skin layer. This layer formed relatively quickly but slowed down subsequent sintering, as the direct interaction of the plasma with the buried layer of unsintered material was impeded. The interaction remained on the top surface, leading to a temperature increase and the subsequent conduction of the generated heat to the underlying nanoparticles. While this resulted in a medium drop in effective resistivity, the adhesion of the tracks was often insufficient as the particles did not result in sufficient anchoring to the substrate [36]. The immediate conclusion from this data is the limitation of processable thicknesses using low-pressure plasma reactors.

The major drawback of utilizing an evacuated processing vessel was alleviated by the introduction of atmospheric plasma jet technologies. In order to create a plasma in these systems, often dielectric barrier discharges in a confined space are employed. The ionized species generated in the limited gas volume are then convectively directed toward the substrate. Wünscher *et al.* showed the application of an argon plasma torch for the generation of conductive structures at atmospheric pressures. The nonthermal plasma showed a relatively strong interaction with the deposit and resulted in conductivities of up to 12% of bulk silver [20].

One of the decisive questions for the application in the production of functional thin films is the suitability for higher throughput and larger area applications. With the application of plasma jets, this has come a long way from long sintering times in evacuated vessels. Hybrid techniques, such as the usage of plasma sintering in combination with microwave flash sintering, alleviate the temporal limitations while providing reasonable adhesion.

2.3.6 Sintering Using Electromagnetic Fields

One broad class of sintering approaches comprises attempts to use electromagnetic (EM) radiation from ultraviolet (UV) to microwave wavelengths in order to couple energy into printed structures and generate heat selectively. The absorption of the materials present in the processing chamber, however, plays a vital role in the efficiency of the process and, hence, its selectivity (cf. Table 2.1). Electromagnetic sintering approaches include impulse light processing [51, 52, 71, 72], laser sintering [42, 73–75], IR sintering [76, 77], UV or UV-assisted [78] sintering as well as microwave sintering [40, 41].

Table 2.1 Commonly used electromagnetic radiation, their wavelength, and their main mechanism of interaction required for sintering.

EM	Wavelength	Materials	Interaction
UV	180–400 nm	Precursor, NP	Breakdown of organic constituents, surface energy–driven sintering
VIS	400–700 nm	NP	Thermal sintering with selectivity due to absorption spectra
IR	0.7–40 μm	Precursor, NP	Thermal sintering, integral heating with different penetrations into the substrate based on the wavelength used
MW	0.01–1 m	NP	Thermal sintering, selectivity through differences in $\tan \delta$ and coupling
DC	–	NP	Thermal sintering, selectivity through differences in $\tan \delta$ and coupling

The interaction of electromagnetic waves with matter can generate various effects, as the interaction is based on both the frequency-dependent conductive and the dielectric characteristics of materials. These can be coupled to the present fields using Maxwell's equations [79]. As a result of the field distribution inside the sample, energy of the amount w , which is proportional to the squared magnitudes of the alternating field components, will be released locally [80].

$$w = \frac{\omega}{2} (\epsilon_0 \Im\{\epsilon_r\} \mathbf{E}^2 + \mu_0 \Im\{\mu_r\} \mathbf{H}^2) \quad (2.5)$$

here ω is the angular frequency, ϵ denotes the dielectric permittivity, μ the magnetic permeability, $\Im$ the imaginary part, $\mathbf{E}$ the electric field, and $\mathbf{H}$ denotes the magnetic field vector, respectively. The subscripts “0” and “ r ” denote the free space and the frequency-dependent relative material values, respectively. The aforementioned equation furthermore allows for the reduction to the limiting low-frequency case where $\omega\epsilon_0\Im\{\epsilon_r\}$ reduces to the electric conductivity σ of the material and hence Joule heating can be observed with the magnitude of $\sigma\mathbf{E}^2$.

The given equation enables a first-order interpretation of the physical meaning of the interaction of materials with the radiation and clearly shows that, for the desired application to selectively couple energy in deposits in a multimaterial stack, the overlap in the absorption spectra needs to be minimized. This is often very challenging as absorption characteristics change during processing, where, for example, the absorption of a growing particle or cluster during the illumination with visible light results in a thermal runaway due to the strongly enhanced dissipation of energy [71]. Similar effects can also be found in the application of microwave energy to nanoparticle deposits.

The efficiency of the absorption of the radiation also relates to the size of the deposits with respect to penetration of EM fields into conductive particles, which is generally described by the so-called skin depth. In order to couple and dissipate energy in conductive structures, a critical size needs to be exceeded, as particles much smaller than the skin depth δ_s appear transparent for the respective

radiation. As the skin depth δ_s is defined as $\sqrt{2/(\omega\sigma\mu_0\mu_r)}$, one can deduce the influence of the frequency of the applied field on the absorption characteristics. For instance, silver nanoparticles are essentially transparent to microwave ($\delta_s \approx 1 \mu\text{m}$) radiation until a certain level of aggregation has occurred and the absorption swiftly increases [81].

Typical substrates for printed conductors comprise polymer foils such as poly(ethylene terephthalate) (PET), poly(ethylene naphthalate) (PEN), polycarbonate (PC), or polyimide (PI). All of these exhibit strong absorption in the UV wavelengths, while PI has additional absorption components in the visible spectrum, giving rise to its characteristic coloring. It has been shown that the influence of the substrate cannot be neglected for the sintering using pulsed visible light [71]. The effects include the damping of the blue spectral components, preventing *thermal runaway*, as well as slight increase in substrate temperatures, which omitted the redeposition of evaporated solvent. By tuning the substrate or substrate holder, the transient of sintering can be guided and optimal results may be obtained.

2.3.6.1 Impulse Light Sintering

Impulse light sintering is a special version of photonic curing, where the energy is supplied to the substrate by a pulsed, broadband, high-energy illumination such as a xenon arc lamp [46, 72, 82]. The spectra of such lamps typically span a large part of the electromagnetic spectrum from ultraviolet through the visible range all the way into the infrared region (approximately 200–1200 nm). In order to enhance selectivity, typically spectral filters are employed to reduce the amount of UV radiation as substrates such as polymer foils exhibit relatively strong absorption in this band. At the same time not only metallic materials with absorption characteristics in the visible range such as copolymers [83], conductive adhesives [84], or sol–gel dielectrics [85] may be processed.

The broad spectrum allows for the processing of a lot of different metallic materials, which in the nanometer range exhibit suitable plasmon resonances. Furthermore, shifts, as a result of particle growth, can be tolerated and do not require an adjustment of the illumination. The extremely high temperature generated during the micro- to millisecond time frames enable the detachment as well as evaporation of polymeric constituents and enable particle interaction with strong material transport. The selection of pulse duration, amplitude, and repetition frequency needs to be performed very carefully in order to obtain reliable results. In insufficiently tuned systems, the interaction may be so strong, that all the binder, which occasionally facilitates the adhesion to the underlying substrate, is removed resulting in poor adhesion or blow-off of the deposit from the substrate.

This approach has been commercialized by a number of different suppliers delivering systems with sheet-to-sheet or roll-to-roll compatibility [86–89]. Special techniques such as pulse shaping, where the amplitude and duration of pulses within a pulse train may be adjusted down to timescales of tens of microseconds, allow to steer the temperature profile in the illuminated structure and, hence, prevent explosive evaporation of wet deposits [90] or enable optimal

curing without overly strong interaction of the strongly heated deposit with the underlying materials. Multimaterial stacks present much bigger challenges than simple two-material systems of substrate and ink, as the absorptivity, the thermal resistance and capacitance of the different layers start to play a major role (cf. Section 2.3.6.3).

Intense light processing is, in the current state of the art, one of the few technologies that can provide suitable results for roll-to-roll processing, with challenges mainly found in the need for drying as well as multilayer processing. The wall-plug efficiency of the equipment is normally higher than that of most laser sintering systems. While providing high processing speed, both the total cost of ownership and the operating costs are in some cases limiting its application.

2.3.6.2 Microwave Sintering

Microwave sintering has attracted considerable attention as a selective sintering technique [40, 41, 91]. Especially the method known as *microwave flash sintering* allows for the rapid processing of dry, presintered structures without any noticeable effect on the substrate [40]. In this technique, a hybrid approach is employed, where a first step enables the creation of initial conduction paths or aggregation throughout the printed structure in order to trigger noticeable absorption, whereas microwave sintering as a second step allows for the swift reduction of the feature's resistance.

A short thermal treatment (1–5 min at 110 °C) generated structures exhibiting low conductivity. It was found that the magnitude of initial resistance and hence the degree of cluster/percolation path formation related to the efficiency of the microwave treatment, yielding low resistance for structures only if the initial resistance was below a threshold resistance. A higher resistance, however, could be partially compensated by a longer microwave processing time. Hence, the threshold resistance may be increased from 10^5 to $10^7 \Omega$ when treatment times are adapted to 1 and 60 s, respectively. The different thresholds illustrate the relation between the state of sintering or aggregation prior to microwave processing as larger clusters are formed during the initial step. Hence, the absorption increased dramatically resulting in strong local heating and in turn a decrease in resistance of up to four orders of magnitude.

The process lends itself to optimization as both the presintering and the microwave heating step can be used to shorten the overall sintering time and improve the overall performance. Photonic drying/presintering was employed, reducing the overall time required to less than 60 s, by way of generating structures readily susceptible to microwave energy. It was even found that photonic presintered structures were more susceptible to MW radiation compared to their thermally sintered counterparts. This indicates the generation of larger initial structures available for strong microwave absorption. Also, focusing the electric fields by means of antennae was described allowing for improved local sintering.

A major challenge that remains for this technique is the generation of highly homogeneous fields in large-scale applications with locally varying multimaterial stacks.

2.3.6.3 Influence of the Substrate

Even though the selective coupling of the radiation into the printed ink pattern renders the process selective, the stack of substrate material plays a decisive role especially during pulsed sintering.

Most important are the temperature profiles both in the ink pattern, the substrate and at their interface. Wünscher *et al.* presented a straightforward estimation of the timescales involved in photonic sintering by comparing the thermal equilibrium timescales τ for the ink (i) and the substrate (s). By considering the specific heat capacities c_p , the densities ρ , the thicknesses x and the thermal conductivities κ the pulse width t_{pulse} should fulfill the following condition:

$$\underbrace{\frac{c_{p,i}\rho_i x_i^2}{4\kappa_i}}_{\tau_{\text{ink}}} \ll t_{\text{pulse}} \ll \underbrace{\frac{c_{p,s}\rho_s x_s^2}{4\kappa_s}}_{\tau} \text{substrate} \quad (2.6)$$

When comparing typical values τ_i and τ_s it becomes evident that the values for ink are in the microsecond range, while substrates exhibit typical values in the millisecond range. Therefore, in order to omit overwhelmingly strong heating of the substrate, pulse lengths should be in the sub-millisecond range with time delays between subsequent pulses in the tens to hundreds of milliseconds. Of course, in a very well-controlled process, the repetition rate and/or amplitudes of the applied energy may be used to generate distinct temperature transients in the deposit without overheating the substrate [90].

It furthermore needs to be considered that a multimaterial stack and the substrate holder itself may absorb the radiation and hence alter the performance of the sintering step. Many of the photonic setups employ mirrors for the focusing of the radiation onto the substrate and reflection at the substrate holder, so that high energy radiation may pass the sample multiple times before being fully absorbed. By using differently absorbing substrate materials, a change in the conductivity transitions during low-frequency *wet*, that is, combining drying and sintering in one process step, photonic sintering of silver nanoparticle inks was shown. A blue reflector under the transparent substrate was thereby found to be optimal, as it repeatedly reflects the wavelengths where nanoparticles in the deposit absorb strongest and hence form a consistently sintered track. A red reflector, in contrast, revealed a clear delay in the sintering onset and inconsistent sintering most likely due to overheating when the deposit became susceptible to the resonating waves. As a result, modification of the substrate holder spectral response allowed to sinter silver tracks consistently on transparent substrates without intermediate drying [71].

Another simplified time-dependent model can be deduced using equivalent circuits, as depicted in Figure 2.4. The depicted circuit considers the conduction of the inward heat flux $\dot{Q}_{\text{in}}$, derived, for instance, from Lambert–Beer's law [82, 92], through a material stack consisting of ink (i) on top n layers of substrate (s). The equivalent thermal impedance of the substrate Z_s has a decisive role on the temperature evolution inside the ink as its heat sink effect may prevent the printed deposit to reach temperatures sufficient for sintering. Niittynen

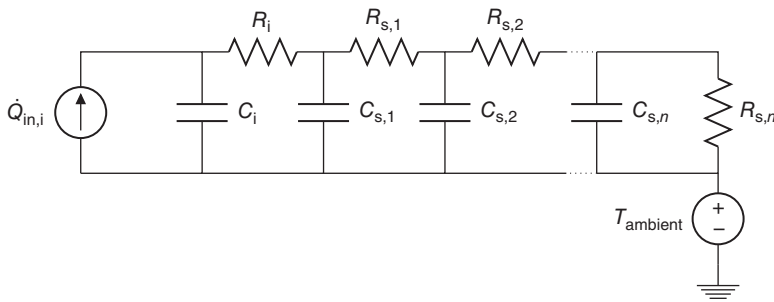


Figure 2.4 Equivalent circuit model for the heat transport through multiple layers of material during photonic sintering. Adapted from Niittynen (2014) [95].

and Mantysalo [93] showed the effect of the low thermal resistance of silicon on the resulting conductivities. The modeling revealed that bare silicon would not allow for laser sintering of deposited silver structures, but the inclusion of a $1\ \mu\text{m}$ silicon oxide layer as thermal barrier would allow for a sufficient temperature increase [94]. Furthermore, the gradient of the ambient temperature T_{ambient} can be included into the model to represent the effects of cooled surfaces.

More elaborate models have been developed over the years in order to allow for better understanding and optimization of systems with variable pulse lengths as well as amplitude modulation.

Furthermore, wetting characteristics during sintering are essential especially in the case of *wet* sintering. Here, the heating rates and the temperature-dependent wetting characteristics of the materials are essential for consistent results. It was shown that by control of the heating rates during photonic sintering of wet deposits, optimal line formation could be preserved [71].

2.4 Conclusion

Industrial inkjet printing has come a long way from a purely graphical technology, delivering high-quality digital print products, toward a production technique in many segments spanning décor, tiles, and printed functionality.

The recent developments have triggered a variety of work toward a more fundamental understanding. This is especially true for the advances in the measurement and modeling of the dynamic effects on ink rheology and surface tension in time scales of a few microseconds. This has substantially simplified the screening and selection of inks, which are better matched to the printheads and allows for a widening of the operational windows or the sophisticated tailoring of driving schemes for functional applications.

As a result, inkjet is now being found in a number of commercial applications, which use the digital and precise application of fluids on flat or patterned surfaces. Examples include metallization and masking in the production of solar cells, imprint lithography, display manufacturing, and OLED manufacturing [96, 97]

Functional printing, which requires highly stable fluid formulations, often requires postprocessing to remove stabilizing agents and establish cohesive

structures. In printing of metal structures, this is typically accomplished by thermal energy assisting the thermodynamic driving forces for atomic motion. The requirements for low-cost substrates alongside with their rather low temperature stability triggered a multitude of sintering approaches, where thermal energy is supplied in a selective manner. Although the lab results with 30–50% of the bulk conductivity are very impressive, many of these technologies are only slowly progressing into feasible industrial processes.

References

- 1 Wijshoff, H. (2008) Structure-and fluid-dynamics in piezo inkjet printheads. PhD thesis. University of Twente.
- 2 Bogy, D. and Talke, F. (1984) Experimental and theoretical study of wave propagation phenomena in drop-on-demand ink jet devices. *IBM J. Res. Dev.*, **28** (3), 314–321.
- 3 Castrejon-Pita, A.A., Castrejon-Pita, J.R., and Hutchings, I.M. (2012) Breakup of liquid filaments. *Phys. Rev. Lett.*, **108** (7), 074506.
- 4 Derby, B. (2011) Inkjet printing ceramics: from drops to solid. *J. Eur. Ceram. Soc.*, **31** (14), 2543–2550.
- 5 Fromm, J.E. (1984) Numerical calculation of the fluid dynamics of drop-on-demand jets. *IBM J. Res. Dev.*, **28** (3), 322–333.
- 6 Vadillo, D.C., Tuladhar, T.R., Mulji, A.C., and Mackley, M.R. (2010) The rheological characterization of linear viscoelasticity for ink jet fluids using piezo axial vibrator and torsion resonator rheometers. *J. Rheol.*, **54** (4), 781–795.
- 7 Vadillo, D.C. and Tembely, M. (2012) The matching of polymer solution fast filament stretching, relaxation, and break up experimental results with 1D and 2D numerical viscoelastic simulation. *J. Rheol.*, **56** (6), 1491.
- 8 Wagner, C., Amarouchene, Y., Bonn, D., and Eggers, J. (2005) Droplet detachment and satellite bead formation in viscoelastic fluids. *Phys. Rev. Lett.*, **95** (16), 164504.
- 9 Morrison, N.F. and Harlen, O.G. (2010) Viscoelasticity in inkjet printing. *Rheol. Acta*, **49** (6), 619–632.
- 10 Hoath, S.D., Hsiao, W.K., Hutchings, I.M., and Tuladhar, T.R. (2014) Jetted mixtures of particle suspensions and resins. *Phys. Fluids*, **26** (10), 101701.
- 11 Hoath, S.D., Hsiao, W.K., Martin, G.D., Jung, S., Butler, S.A., Morrison, N.F., Harlen, O.G., Yang, L.S., Bain, C.D., and Hutchings, I.M. (2015) Oscillations of aqueous PEDOT: PSS fluid droplets and the properties of complex fluids in drop-on-demand inkjet printing. *J. Non-Newtonian Fluid Mech.*, **223**, 28–36.
- 12 Hoath, S.D., Hutchings, I.M., Martin, G.D., Tuladhar, T.R., Mackley, M.R., and Vadillo, D.C. (2009) Links between ink rheology, drop-on-demand jet formation, and printability. *J. Imaging Sci. Technol.*, **53** (4), 041208.
- 13 Hoath, S.D., Harlen, O.G., and Hutchings, I.M. (2012) Jetting behavior of polymer solutions in drop-on-demand inkjet printing. *J. Rheol.*, **56** (5), 1109.
- 14 Toshiba TEC Corporation (2015) Datasheet: CF1 Family.
- 15 Fujifilm-Dimatix (2015) Datasheet: StarFire(TM) SG1024/MC.

- 16 Xaar (2015) Datasheet: Xaar 1002.
- 17 Lee, A., Sudau, K., and Ahn, K. (2012) Optimization of experimental parameters to suppress nozzle clogging in inkjet printing. *Ind. Eng. Chem. Res.*, **51** (40), 13 195–13 204.
- 18 Olkkonen, J., Leppäniemi, J.H., Mattila, T., and Eiroma, K. (2014) Sintering of inkjet printed silver tracks with boiling salt water. *J. Mater. Chem. C*, **2** (18), 3577.
- 19 Layani, M., Grouchko, M., Shemesh, S., and Magdassi, S. (2012) Conductive patterns on plastic substrates by sequential inkjet printing of silver nanoparticles and electrolyte sintering solutions. *J. Mater. Chem.*, **22** (29), 14 349.
- 20 Wünscher, S., Stumpf, S., Teichler, A., Pabst, O., Perelaer, J., Beckert, E., and Schubert, U.S. (2012) Localized atmospheric plasma sintering of inkjet printed silver nanoparticles. *J. Mater. Chem.*, **22** (47), 24569.
- 21 Moon, K.S., Dong, H., Maric, R., Pothukuchi, S., Hunt, A., Li, Y., and Wong, C.P. (2005) Thermal behavior of silver nanoparticles for low-temperature interconnect applications. *J. Electron. Mater.*, **34** (2), 168–175.
- 22 Felba, J., Nitsch, K., Piasecki, T., Paluch, P., Moscicki, A., and Kinart, A. (2009) The influence of thermal process on electrical conductivity of microstructures: made by ink-jet painting with the use of ink containing nano sized silver particles. 2009 9th IEEE Conference on Nanotechnology (IEEE-NANO), vol. 8, pp. 408–411.
- 23 Shin, D.Y., Jung, M., and Chun, S. (2012) Resistivity transition mechanism of silver salts in the next generation conductive ink for a roll-to-roll printed film with a silver network. *J. Mater. Chem.*, **22** (23), 11 755.
- 24 Dearden, A.L., Smith, P.J., Shin, D.Y.Y., Reis, N., Derby, B., and O'Brien, P. (2005) A low curing temperature silver ink for use in ink-jet printing and subsequent production of conductive tracks. *Macromol. Rapid Commun.*, **26** (4), 315–318.
- 25 Smith, P.J., Shin, D.Y., Stringer, J.E., Derby, B., and Reis, N. (2006) Direct ink-jet printing and low temperature conversion of conductive silver patterns. *J. Mater. Sci.*, **41** (13), 4153–4158.
- 26 Felba, J., Nitsch, K., Piasecki, T., Tesarski, S., Moscicki, A., Kinart, A., Bonfert, D., and Bock, K. (2009) Properties of conductive microstructures containing nano sized silver particles. Proceedings of the Electronic Packaging Technology Conference, EPTC, pp. 879–883.
- 27 Magdassi, S., Grouchko, M., Berezin, O., and Kamyshny, A. (2010) Triggering the sintering of silver nanoparticles at room temperature. *ACS Nano*, **4** (4), 1943–1948.
- 28 Zapka, W., Voit, W., Loderer, C., and Lang, P. (2008) Low temperature chemical post-treatment of inkjet printed nano-particle silver inks. International Conference on Non Impact Printing and Digital Fabrication.
- 29 Grouchko, M., Kamyshny, A., Mihailescu, C.F., Anghel, D.F., and Magdassi, S. (2011) Conductive inks with a “built-in” mechanism that enables sintering at room temperature. *ACS Nano*, **5** (4), 3354–3359.
- 30 Wünscher, S., Abbel, R., Perelaer, J., and Schubert, U.S. (2014) Progress of alternative sintering approaches of inkjet-printed metal inks and their

- application for manufacturing of flexible electronics. *RSC Adv.*, **2**, 10 232–10 261.
- 31 Ruschau, G.R., Yoshikawa, S., and Newnham, R.E. (1992) Resistivities of conductive composites. *J. Appl. Phys.*, **72** (3), 953–959.
 - 32 Wu, W., Brongersma, S.H., Van Hove, M., and Maex, K. (2004) Influence of surface and grain-boundary scattering on the resistivity of copper in reduced dimensions. *Appl. Phys. Lett.*, **84** (15), 2838–2840.
 - 33 de Vries, J.W.C. (1988) Resistivity of thin Au films as a function of grain diameter and temperature. *J. Phys. F: Metal Phys.*, **18** (2), 515.
 - 34 Wünscher, S., Stumpf, S., Perelaer, J., and Schubert, U.S. (2014) Towards single-pass plasma sintering: temperature influence of atmospheric pressure plasma sintering of silver nanoparticle ink. *J. Mater. Chem. C*, **2**, 1642.
 - 35 Reinhold, I., Hendriks, C.E., Eckardt, R., Kranenburg, J.M., Perelaer, J., Baumann, R.R., and Schubert, U.S. (2009) Argon plasma sintering of inkjet printed silver tracks on polymer substrates. *J. Mater. Chem.*, **19** (21), 3384.
 - 36 Niittynen, J., Halonen, E., and Mäntysalo, M. (2011) Conductivity and Adhesion Study of Plasma-sintered Nanoparticle Silver Ink. LOPEC, pp. 134–138.
 - 37 Jang, S., Lee, D.J., Lee, D., and Oh, J.H. (2013) Electrical sintering characteristics of inkjet-printed conductive Ag lines on a paper substrate. *Thin Solid Films*, **546**, 157–161.
 - 38 Allen, M.L., Aronniemi, M., Mattila, T., Alastalo, A., Ojanperä, K., Suhonen, M., and Seppä, H. (2008) Electrical sintering of nanoparticle structures. *Nanotechnology*, **19** (17), 175 201.
 - 39 Alastalo, A., Seppä, H., Leppäniemi, J.H., Aronniemi, M., Allen, M.L., and Mattila, T. (2010) Modelling of nanoparticle sintering under electrical boundary conditions. *J. Phys. D: Appl. Phys.*, **43** (48), 485 501.
 - 40 Perelaer, J., Klokkenburg, M., Hendriks, C.E., and Schubert, U.S. (2009) Microwave flash sintering of inkjet-printed silver tracks on polymer substrates. *Adv. Mater.*, **21**, 4830–4834.
 - 41 Perelaer, J., Abbel, R., Wünscher, S., Jani, R., van Lammeren, T.J., and Schubert, U.S. (2012) Roll-to-roll compatible sintering of inkjet printed features by photonic and microwave exposure: from non-conductive ink to 40% bulk silver conductivity in less than 15 seconds. *Adv. Mater.*, **24** (19), 2620–2625.
 - 42 Choi, J.H., Ryu, K., Park, K., and Moon, S.J. (2015) Thermal conductivity estimation of inkjet-printed silver nanoparticle ink during continuous wave laser sintering. *Int. J. Heat Mass Transfer*, **85**, 904–909.
 - 43 Cherrington, M., Claypole, T., Gethin, D., Worsley, D., and Deganello, D. (2012) Non-contact assessment of electrical performance for rapidly sintered nanoparticle silver coatings through colorimetry. *Thin Solid Films*, **522**, 412–414.
 - 44 Chung, W.H., Hwang, H.J., Lee, S.H., and Kim, H.S. (2013) In situ monitoring of a flash light sintering process using silver nano-ink for producing flexible electronics. *Nanotechnology*, **24** (3), 035 202.
 - 45 Polzinger, B., Schoen, F., Matic, V., Keck, J., Willeck, H., Eberhardt, W., and Kueck, H. (2011) UV-sintering of inkjet-printed conductive silver tracks. 2011 11th IEEE International Conference on Nanotechnology, pp. 201–204.

- 46 Hösel, M. and Krebs, F.C. (2012) Large-scale roll-to-roll photonic sintering of flexo printed silver nanoparticle electrodes. *J. Mater. Chem.*, **22** (31), 15 683–15 688.
- 47 Chiolerio, A., Maccioni, G., Martino, P., Cotto, M., Pandolfi, P., Rivolo, P., Ferrero, S., and Scaltrito, L. (2011) Inkjet printing and low power laser annealing of silver nanoparticle traces for the realization of low resistivity lines for flexible electronics. *Microelectron. Eng.*, **88** (8), 2481–2483.
- 48 Yung, K., Gu, X., Lee, C., and Choy, H. (2010) Ink-jet printing and camera flash sintering of silver tracks on different substrates. *J. Mater. Process. Technol.*, **210** (15), 2268–2272.
- 49 Fang, Z.Z. and Wang, H. (2010) *Sintering of Advanced Materials*, Woodhead Publishing, Cambridge, UK.
- 50 Nanda, K.K. (2009) Size-dependent melting of nanoparticles: hundred years of thermodynamic model. *Pramana - J. Phys.*, **72** (4), 617–628.
- 51 West, J., Sears, J., Smith, S., and Carter, M. (2010) Photonic sintering - an example: photonic curing of silver nanoparticles. *Sintering of Advanced Materials - Fundamentals and Processes*, pp. 275–288.
- 52 Drahi, E., Blayac, S., Borbély, A., Benaben, P., and Borbely, A. (2015) Impact of ink synthesis on processing of inkjet-printed silicon nanoparticle thin films: a comparison of Rapid Thermal Annealing and photonic sintering. *Thin Solid Films*, **574**, 169–176.
- 53 Soltman, D., Smith, B., Kang, H., Morris, S.J.S., and Subramanian, V. (2010) Methodology for inkjet printing of partially wetting films. *Langmuir*, **26** (19), 15686–15693.
- 54 Kang, H., Soltman, D., and Subramanian, V. (2010) Hydrostatic optimization of inkjet-printed films. *Langmuir*, **26** (13), 11568–11573.
- 55 Soltman, D. and Subramanian, V. (2008) Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir*, **24** (5), 2224–2231.
- 56 Deegan, R.D., Bakajin, O., Dupont, T.F., Huber, G., Nagel, S.R., and Witten, T.A. (1997) Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, **389** (6653), 827–829.
- 57 Talbot, E., Berson, A., Brown, P., and Bain, C. (2012) Drying and deposition of picolitre droplets of colloidal suspensions in binary solvent mixtures. International Conference on Non Impact Printing and Digital Fabrication.
- 58 Perelaer, J., Smith, P.J., Hendriks, C.E., van den Berg, A.M.J., and Schubert, U.S. (2008) The preferential deposition of silica micro-particles at the boundary of inkjet printed droplets. *Soft Matter*, **4** (5), 1072.
- 59 Kajiya, T. and Kobayashi, W. (2009) Controlling the drying and film formation processes of polymer solution droplets with addition of small amount of surfactants. *J. Phys. Chem. B*, **113** (47), 15460–15466.
- 60 Abbel, R., Teunissen, P., Michels, J., and Groen, W.A. (2014) Narrow conductive structures with high aspect ratios through single-pass inkjet printing and evaporation-induced dewetting. *Adv. Eng. Mater.*, **17** (5), 615–619.
- 61 Farraj, Y., Grouchko, M., Magdassi, S., Koch, F., Wittkötter, M., Müller, M., Reinhold, I., and Zapka, W. (2014) Ink-jet printed copper complex MOD ink for plastic electronics. International Conference on Non Impact Printing and Digital Fabrication.

- 62 Ingham, B., Lim, T.H., Dotzler, C.J., Henning, A., Toney, M.F., and Tilley, R.D. (2011) How nanoparticles coalesce: an in situ study of Au nanoparticle aggregation and grain growth. *Chem. Mater.*, **23** (14), 3312–3317.
- 63 Greer, J.R. and Street, R.A. (2007) Mechanical characterization of solution-derived nanoparticle silver ink thin films. *J. Appl. Phys.*, **101** (10), 103529.
- 64 Chou, K.S., Huang, K.C., and Lee, H.H. (2005) Fabrication and sintering effect on the morphologies and conductivity of nano-Ag particle films by the spin coating method. *Nanotechnology*, **16** (6), 779–784.
- 65 Wakuda, D., Hatamura, M., and Suganuma, K. (2007) Novel method for room temperature sintering of Ag nanoparticle paste in air. *Chem. Phys. Lett.*, **441** (4–6), 305–308.
- 66 Layani, M. and Magdassi, S. (2011) Flexible transparent conductive coatings by combining self-assembly with sintering of silver nanoparticles performed at room temperature. *J. Mater. Chem.*, **21** (39), 15 378.
- 67 Gautrein, A., Schmiga, C., Glatthaar, M., Tremel, W., and Glunz, S. (2014) Nanometallic silver inks for metallization of ITO-coated silicon solar cells: influence of organic components. 29th European Photovoltaic Solar Energy Conference and Exhibition, EU PVSEC, Amsterdam, The Netherlands, September 2014, pp. 22–26.
- 68 Liebermann, M.A. and Lichtenberg, A.J. (1994) *Principles of Plasma Discharges and Materials Processing*, John Wiley & Sons, Inc., Hoboken, New Jersey.
- 69 Perelaer, J., Jani, R., Grouchko, M., Kamysny, A., Magdassi, S., and Schubert, U.S. (2012) Plasma and microwave flash sintering of a tailored silver nanoparticle ink, yielding 60% bulk conductivity on cost-effective polymer foils. *Adv. Mater.*, **24** (29), 3993–3998.
- 70 Perelaer, J., Wünsch, S., Wolf, F.M., Abbel, R., Grouchko, M., Magdassi, S., and Schubert, U.S. (2013) Low temperature sintering of inkjet printed metal precursor inks for organic electronic applications. International Conference on Non Impact Printing and Digital Fabrication, pp. 359–362.
- 71 Reinhold, I., Müller, M., Müller, M., Voit, W., and Zapka, W. (2012) Spectrally enhanced photonic sintering. International Conference on Non Impact Printing and Digital Fabrication, IS&T, Quebec, CA.
- 72 Abbel, R., van Lammeren, T., Hendriks, R., Ploegmakers, J., Rubingh, E.J., Meinders, E.R., and Groen, W.A. (2012) Photonic flash sintering of silver nanoparticle inks: a fast and convenient method for the preparation of highly conductive structures on foil. *MRS Commun.*, **2** (04), 145–150.
- 73 Lee, D.G., Kim, D.K., Moon, Y.J., and Moon, S.J. (2013) Effect of temperature on electrical conductance of inkjet-printed silver nanoparticle ink during continuous wave laser sintering. *Thin Solid Films*, **546**, 443–447.
- 74 Niittynen, J., Sowade, E., Kang, H., Baumann, R.R., and Mäntysalo, M. (2015) Comparison of laser and intense pulsed light sintering (IPL) for inkjet-printed copper nanoparticle layers. *Sci. Rep.*, **5**, 8832.
- 75 Kumpulainen, T., Pekkanen, J., Valkama, J., Laakso, J., Tuokko, R., and Mäntysalo, M. (2011) Low temperature nanoparticle sintering with continuous wave and pulse lasers. *Opt. Laser Technol.*, **43** (3), 570–576.

- 76 Tobjörk, D., Aarnio, H., Pulkkinen, P., Bollström, R., Määttänen, A., Ihalainen, P., Mäkelä, T., Peltonen, J., Toivakka, M., Tenhu, H., and Österbacka, R. (2012) IR-sintering of ink-jet printed metal-nanoparticles on paper. *Thin Solid Films*, **520** (7), 2949–2955.
- 77 Denneulin, A., Blayo, A., Neuman, C., and Bras, J. (2011) Infra-red assisted sintering of inkjet printed silver tracks on paper substrates. *J. Nanopart. Res.*, **13** (9), 3815–3823.
- 78 Jahn, S.F., Blaudeck, T., Baumann, R.R., Jakob, A., Ecorchard, P., Rüffer, T., Lang, H., and Schmidt, P. (2010) Inkjet printing of conductive silver patterns by using the first aqueous particle-free MOD ink without additional stabilizing ligands. *Chem. Mater.*, **22** (10), 3067–3071.
- 79 Fang, X., Deng, Y., and Li, J. (2015) Plasmon resonance and heat generation in nanostructures. *Math. Methods Appl. Sci.*, **38** (18), 4663–4672.
- 80 Rybakov, K.I., Semenov, V.E., Egorov, S.V., Ereemeev, A.G., Plotnikov, I.V., and Bykov, Y.V. (2006) Microwave heating of conductive powder materials. *J. Appl. Phys.*, **99** (2), 023506.
- 81 Figueroa, M., Schraer, S., Pourrezaei, K., and Tyagi, S. (2012) Surface enhanced Raman scattering and microwave absorption in silver nanoparticle inks. *Plasmonics in Biology and Medicine IX*, vol. 8234, pp. 82 340A–82 340A–6.
- 82 West, J., Sears, J., Smith, S., and Carter, M. (2010) *Sintering of Advanced Materials*, Woodhead Publishing.
- 83 Helgesen, M., Carlé, J.E., Andreassen, B., Hösel, M., Norrman, K., Søndergaard, R.R., and Krebs, F.C. (2012) Rapid flash annealing of thermally reactive copolymers in a roll-to-roll process for polymer solar cells. *Polym. Chem.*, **3** (9), 2649.
- 84 Cui, H.W., Jiu, J.T., Nagao, S., Sugahara, T., Suganuma, K., Uchida, H., and Schroder, K.A. (2014) Ultra-fast photonic curing of electrically conductive adhesives fabricated from vinyl ester resin and silver micro-flakes for printed electronics. *RSC Adv.*, **4** (31), 15914–15922.
- 85 Tetzner, K., Schroder, K.A., and Bock, K. (2014) Photonic curing of sol-gel derived HfO₂ dielectrics for organic field-effect transistors. *Ceramics International*, **40** (10), 15753–15761.
- 86 Technology, D.T.F. (2015) Datasheet: FLA Lab-240c.
- 87 Novacentrix (2015) Datasheet: PulseForge® 3300.
- 88 Xenon (2015) Datasheet: Xenon(TM) S-5100.
- 89 Kroenert, U., Brown, M., and Woffendin, J. (2014) Customized Solutions for Rapid Photonic Processing. Tech. Rep., Heraeus Noblelight Ltd., www.heraeus-noblelight.com.
- 90 Reinhold, I., Voit, W., Rawson, I., Martin, K., Farnsworth, S., Zapka, W., and Munson, C. (2013) Novel developments in photonic sintering of inkjet printed functional inks. International Conference on Non Impact Printing and Digital Fabrication, pp. 2–4.
- 91 Perelaer, J., DeGans, B.J., and Schubert, U.S. (2006) Ink-jet printing and microwave sintering of conductive silver tracks. *Adv. Mater.*, **18** (16), 2101–2104.

- 92 Guillot, M.J., Schroder, K.A., and McCool, S.C. (2012) Simulating the thermal reponse of thin films during photonic curing. 12th International Conference on Nuclear Engineering, Houston, TX, pp. 1–9.
- 93 Niittynen, J. and Mantysalo, M. (2014) Characterization of laser sintering of copper nanoparticle ink by FEM and experimental testing. *IEEE Trans. Compon. Packag. Manuf. Technol.*, **4** (12), 2018–2025.
- 94 Soltani, A., Kumpulainen, T., and Mäntysalo, M. (2014) Inkjet printed nano-particle Cu process for fabrication of re-distribution layers on silicon wafer. Electronic Components and Technology Conference (ECTC), pp. 1685–1689.
- 95 Niittynen, J. (2014) Equivalent Circuit Modeling of Laser Sintering of Inkjet Printed Lines. Tech. Rep., University of Tampere, Finland.
- 96 Bruner, S., Xu, D., and Phillips, C. (2007) Drop landing accuracy improvements in inkjet printed OLED displays. *SID Symp. Dig. Tech. Pap.*, **38** (1), 1611–1612.
- 97 Crankshaw, M., Goddard, S., Dowling, M., Webb, L., Wild, B., Isaac, J., Creighton, C., and Burton, E. (2008) Inkjet printing of swathe-free displays. International Conference on Non Impact Printing and Digital Fabrication, pp. 736–739.

3

Electroless Plating and Printing Technologies

Yosi Shacham-Diamand, Yelena Sverdlov, Stav Friedberg, and Avi Yaverboim

3.1 Introduction

Electroplating and printing are well-established technologies, both of which have been widely used for various applications. Usually, they are used separately, printing for pattern definition and plating for the deposition of metals. Combining these two methods offers a new additive patterning method that can replace conventional metallization methods for various applications using both 2D and 3D printing.

The most common way to define metal patterns for various applications, that is, integrated circuits, printed circuit boards, electronic packaging, solar cells, flexible electronics, and so on, is by negative patterning. In a typical negative patterning process, the metal is blanket-deposited first. Next, a photoresist, which is a light-sensitive material, is deposited over the metal film. The resist is exposed (e.g., by photons or electrons) and developed, removing the exposed (in positive resist) or unexposed (in negative resists) patterns. Finally, the metal is etched and the resist is removed, leaving behind patterned metal lines and/or pads. An alternative method for metal patterning is positive patterning, for example, the “Lift-off” and the Damascene processes. In the Damascene process, the pattern is defined first as trenches in the interlevel dielectric, the metal is blanket-deposited and removed by chemical mechanical polishing [1]. This way metal lines and pads remain in the predefined trenches.

In this chapter, we describe another positive patterning method, using printing and electroless plating, which allows rapid and low-cost metallization for various applications such as flexible electronics and 3D objects. Recent advances in material printing (see, e.g., [2]) allow direct deposition of patterned catalytic layers serving as a seed for metal nucleation and growth, thus allowing positive patterning of metals. For example, inkjet printing (IJP) of nanoparticles conductive ink has been widely studied for additive fabrication of conductive layers such as for interconnects and contacts. However, most conductive inks are sintered at elevated temperatures, thus limiting the use of those inks for most polymers and papers. High-temperature sintering in air may oxidize copper, which is the most common metal for conductor in electronics, thus silver or other noble metals (Pt, Pd, or Au) should be used for the ink. Alternatively,

vacuum sintering or oxygen- and humidity-free ambient is required to prevent the oxidation of copper, which requires special equipment, making it a less favorable approach, especially for large-size applications. Using polymer or paper substrates limits the maximum anneal temperature, which is a problem since low-temperature annealing results in high metal resistivity. Adding an electroless deposition step allows low-temperature processing yielding low-resistivity interconnects.

A very attractive method for low-cost metallization of flexible devices on plastic or paper is to use electroless deposition, which is a very selective method that can provide high-quality thin films. Electroless deposition does not require external electrical current supply and the deposition is only on the printed seed. With this method, isolated metal patterns can be defined by metal seed printing. The deposited electroless plating increases the interconnect conductivity, improves the mechanical properties of the printed line, improves its reliability, and increases its capability for soldering and bonding capabilities. Combining plating and printing became advantageous with the progress of flexible electronics and manufacturing of large-area displays.

Electroplating had been known for hundreds of years ago, while electroless deposition (ELD) was introduced about 100 years ago [3, 4]. Recently, ELD was applied to micro- and nanoscale technologies [5–7]. Printing is even an older technique with numerous approaches, which are mostly applied for graphics and characters on papers, glass, or other solid surfaces. Recently, 3D printing and printing functional materials have emerged for various applications such as foldable displays, flexible sensors, and even printing organs and components for medical applications [8, 9].

Taking into consideration the recent works on integrating electroless plating with printing, we present here a review of the general concepts, some examples, and a discussion. The generally accepted vision regarding the roadmap of functional printing and the interaction with electrochemical micro- and nanotechnologies in general and plating in particular is presented here. Following a brief review of the dominant methods and tools, we describe the functional printing used for electroless plating seeding and its potential application for 2D, 2.5D, and 3D printing of passive and active components. We specifically describe

Table 3.1 Reasons for combining electroless plating with printing.

Reason	Comment
1. Increase conductivity	Assuming fully grown electroless metal
2. Add mechanical strength	Less porous
3. Compatibility with standard bonding techniques	Withstand the bonding process; better integration
4. Low-temperature process	The alternative is screen printing that requires high-temperature firing or laser anneal
5. Improving optical properties, such as reflectivity	Brighter surface (with additives)

Table 3.2 Problems that arise from combining electroless plating with printing.

Problem	Comment
1. Line shortening	Shunts and leakage current problems
2. Damaging the substrate	Defects formation
3. Damaging electronic devices	– Introduction of mobile alkali ions into the gate or field oxides causing junction leakage and/or threshold voltage shift – Introduction of hydroxyl ions that may affect the dielectric properties of the gate or field dielectrics

the chemical and physical issues in depositing catalytic layers by printing and some approaches that allow good quality seeding. We present few schemes using electroless plating and electroplating. As an example we show the use of printed silver nanoparticle seed for electroless plating of few metals and their alloys. Special attention is given to materials used in 3D printing, which pose some severe plating challenges.

The main highlights of integrating printing with electroless plating are presented in Table 3.1.

However, no technology is without compromises, and combining electroless plating and printing is not an exception. The key problems that may arise from the integration of such technologies are presented in Table 3.2.

Electroless plating can be combined with many printing methods in addition to the inkjet method:

- 1) Laser processing: for example, laser ablation, laser-induced-damage in glass-damage
- 2) Nanoimprinting
- 3) Nanoparticle-activated surfaces: gold NPs on SAM, supersonic beam cluster deposition, and so on
- 4) Deposition on 3D polymer printing
- 5) Deposition on 3D metal printing.

In this chapter, we review the overall integrated process from the substrate selection, seed printing methods, electroless plating, and postprocessing issues. Our main review is about inkjet-printed seed, which is the one mostly used today. The conclusions from IJP can be also applied to other printing methods. However, some problems are unique to IJP mainly because the ink specifications must be suitable for the jetting process, which pose constraints in optimizing the metal deposit.

This section includes the following subsections:

- 1) Electroless plating overview: The electroless preprocess, its chemical and electrochemical basics, and its main applications.
- 2) Functional printing of seed: Main printed methods that can be used for the deposition of the catalytic seed required for electroless plating.
- 3) Critical review: Technology integration, challenges, and solutions.

3.2 Electroless Plating – Overview

Electroless plating, or electroless deposition (ELD), was used for preparing thin films of metals, such as Cu, Co, Ni, Fe, Ag, Sn, Au, Pt, and Pd, and their alloys. Few electroless metals are described in detail in the book by Mallory and Hadju [3] and in a recent review by Shacham-Diamand *et al.* [4]. A broad review of the chemistry and electrochemistry of electroless plating is also given in the book chapters by Djokić [5], Schlesinger [6], and Dubin [7].

ELD has been widely used in micro- and nanosystem technology (MST and NST) applications. The main advantage of electroless plating is its high selectivity, allowing fabrication of isolated and embedded metal patterns on insulating substrates. Therefore, it is used to produce patterns and features that cannot be produced by the common nonselective deposition methods. Electroless plating was demonstrated in a wide variety of substrates: metals and alloys, glasses, polymers, and even biological material. Electroless plating is being used for many other applications, such as decoration and metal finishing; however, in this chapter, we focus on electroless plating for electronics, as this requires high performance with unique electrical properties in addition to the material properties. For a summary of the highlights and problems of electroless plating, see Tables 3.3 and 3.4.

Table 3.3 Highlights of electroless plating.

Highlight	Comments
Selectivity	Capable to deposit thin films of metal and alloys on insulators; for example, glass, ceramics, and polymers
Conformality	Typically very high Its conformality can be tuned allowing super-conformal plating [10]
Simple	Requires relatively simple deposition tool compared to other metallization techniques

Table 3.4 Problems in electroless plating.

Problems	Comments
Aging of the solution	Bath lifetime might be limited (can be extended with additives)
Reaction by-products affecting the deposition	Reaction “poisoning” and film deterioration
Homogenous nucleation	Particle formation
Nucleation on defects in nonselected regions	Selectivity loss due to random nucleation
Growth retardation	Failure to nucleate on selected regions due to contamination or some other problems with the catalytic surface

Electroless plating is a highly selective, conformal, and low-cost method. However, as simple as it looks, the electroless bath preparation and the deposition process are not trivial. One key problem is the deposition electrolyte is potentially unstable; it is being depleted during plating, and it depends on the substrate catalytic properties. The electroless deposition process itself is rather complex and involves few steps. Modeling of electroless plating includes both the thermodynamic and kinetic considerations. The thermodynamics principles of electroless plating can be explained by the Pourbaix diagrams [11] of both the metal/electrolyte couple and the reducing agent/electrolyte couple. Such diagrams were constructed for numerous metals and the associated reducing agent. Pourbaix diagrams show the regimes where the electroless deposition is possible. Electroless plating depends on the catalytic nature of the substrate and the reducing agent. A detailed list of possible catalytic substrates that can initiate the autocatalytic deposition process appears in the important paper by Ohno [12]. Also, detailed reviews of electroless plating for electronics appear in few papers, for example, [13, 14].

Since the solution is potentially unstable, nucleation can occur spontaneously due to local changes in the pH or due to the reaction by-products, which may react with the metal ions forming insoluble salts. To stabilize deposition by preventing homogenous nucleation in the volume, the metal is being complexed with an organic compound, typically organic acids or their salts. Ammonia and amines are also used for making useful metal complexes.

3.2.1 Electroless Plating – Brief Overview

The term electroless plating is used for three similar deposition processes [3–7]:

- Autocatalytic electroless plating
- Substrate-catalyzed electroless plating
- Galvanic displacement.

The first process is the most relevant to this chapter, as it is a self-perpetuating process allowing relatively thick layers. Table 3.5 describes the main components of an autocatalytic bath. In addition to the main components, providing the metal deposition, there are other components that affect the deposition, called “additives.” These compounds have several roles such as modifying and

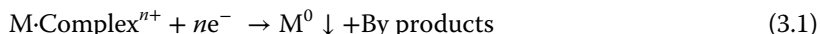
Table 3.5 Electroless plating generic bath components.

Component	Role
Metal salt	Source for the metal
Reducing agent	Metal reduction
Complexing agent	Forms metal–organic complex, prevents homogenous deposition
pH adjustment	Provides proper pH
Buffer	Stabilizes the pH
Additives	Various: levelers, brighteners, accelerators, inhibitors, and so on

improving the mechanical and electrical properties, stabilizing the solution, and inhibiting bath aging or spontaneous degradation. Additives may also be used to modifying texture and morphology, brightening the deposit, promoting dendritic growth, or modifying the conformality of the deposit.

Modeling of the thermodynamics characteristics of electroless plating bath usually follows the “mixed potential theory” [2]. This theory assumes separate paths for the anodic and cathodic partial reactions, similar to that of the Pourbaix theory of corrosion.

The anodic reaction is oxidation of the reducing agent:



The cathodic reaction is that of the metal reduction:



At steady state the anodic current is equal to the cathodic current and the solution becomes at slightly higher potential than that of the electrode where the metal is deposited. The mixed potential theory is a rather simple model based on the thermodynamic characteristics of the reactions. Typically, a more complicated model is required, taking into consideration the interaction between the components at the solution and the surface as well as the kinetic effects.

The deposition reaction and the properties of the deposited material depend greatly on additives. The plating bath usually contains several additives. Although they appear in very minute quantities, they have significant effect on every aspect of the process: deposition rate, bath stability, film appearance, and electrical and mechanical properties. The additives affect nucleation and crystal growth, resulting in a significant change in the deposition rate and the morphology and microstructure of the deposits. Some additives are adsorbed physically or chemically on the surface changing the reaction overpotential. Other additives form a complex with metal ions thus also affecting that overpotential. The additives, even at very low quantities, may have the following effects:

- 1) Surface poisoning, affecting adsorption or surface diffusion, inhibiting the reactions
- 2) Electron transfers, from or toward the electrode, modification; accelerate or decelerate the electrochemical reaction
- 3) Cathodic or anodic current effect due to additive reduction or oxidation
- 4) Microstructure and crystallographic texture modification.

Additives can be organic or inorganic. They may interact or have a joint effect, for example, mixing two additives may yield a different effect than each one of them separately. Additives are designed for specific applications. Therefore, additives for electroless plating on printed seed may differ from additives for another application.

It is unclear yet what additives are useful for integrating electroless plating with printing. The initial printed seed is rather rough and requires some sintering. Therefore, the electroless deposition bath should include some additives for leveling and brightening the deposited metal. In addition, since surface wetting can be an issue, especially for seed on 3D-printed polymer, wetting improvement additives are also required.

3.3 Seed Layer Printing

IJP of nanoparticle conductive ink is widely researched in the additive fabrication of conductive lines for various applications: electronic circuits, solar cells, printed circuit boards, displays, sensors, and more. Recently, it has been demonstrated serving as a seed layer for electroless plating. Practically, inkjet can be applied using few concepts:

- 1) Printing nanoparticle ink: in this case, the ink is serving to print part of the conductor. The electroless plating technology is used for conducting metal deposition. Similar selective process is also used for metal oxides (i.e., ZnO nanowires) by a chemical bath deposition (CBD) for other functions (i.e., sensors) [15]. For example, Co and Ni alloys can be deposited as capping layers against corrosion or as mechanical protection against scratches and wear out. Another example is selective chemical bath deposition of semi-conductor oxide, such as ZnO on printed seed [15].
- 2) Metal ion printing: in this case, the deposited metal is rather thin and it serves mostly as a seed. In this case, the bulk of the conductor is the electroless plated metal. In some cases, if the geometry of the circuits allows it (i.e., if there is a common contact), additional conducting metal is added by electroplating.
- 3) Modified ink with additives: the ink can be modified by components stabilizing the surface and improving adhesion and structural stability. Cheng *et al.* [16] demonstrated adding oligomers, such as vinyl acetate with sulfate group on chain end, that are synthesized by a free-radical polymerization, improving metal ink postjetting properties (i.e., adhesion).

The ink can be applied in various methods. In this chapter, we mostly refer to inkjet-printed material. Here, we discuss some of the problems that are unique to inkjet printing, especially due to the unique features and the constraints on the jetting process, the drop shape, the drying process, and the postdeposition processes. However, many of the problems that are described here are general and relevant to other print methods.

3.4 Electroless Plating on Printed Parts

Electroless plating has been demonstrated with printing numerous times [17]. The common method is to print the catalysts followed by electroless plating. Conventional Cu is deposited on catalytic seed that is defined by microlithography. The seed can be any catalytic metal in bulk, thick, or thin film form. It can be deposited by physical vacuum deposition (PVD) method as well as from liquid by plating or chemical methods. The catalytic material in the solution can be in an ionic form, as is, or in a form of micro or nanoparticles. The seed layer can be patterned using subtractive methods, for example, lithography and etching, or more relevantly to this chapter, by additive methods such as microcontact printing [18, 19] and IJP [20–22]. Typically, palladium (Pd) ions or colloid inks are applied on polymeric substrates before the deposition of copper by electroless plating [23–33]. Further deposition is possible by electroplating.

For example, such a method has been demonstrated by [17] yielding copper metallization with a resistivity of about $2.08 \pm 0.21 \mu\Omega \text{ cm}$ for $>300\text{-nm}$ -thick copper film. However, Pd catalyst is rather expensive and alternatives such as Ag catalyst have been shown to yield good results [34–38]. As is discussed later, the adhesion between the printed seed and the substrate is of prime importance.

There are various solutions including surface treatment, surface functionalization, adding an interface layer, and adding adhesion promoted components to the ink. The key is to keep the seed metal intact during the initial states of the electroless plating while keeping its catalytic properties. After the nucleation and growth stages of the plated metal, the seed layer should not delaminate and withstand the shear stress evolved due to both intrinsic and extrinsic stresses.

There are other advantages of the integration of electroless plating with printing. One advantage, as pointed by Ghosh, for example [39, 40], is the potential cost reduction of a given product compared to that of a thick printed layer. The ink is typically more expensive than plating due to the number of processing steps associated with synthesis, dispersion, purification, and concentration.

The integration of electroless plating with printing usually follows the sequence shown in Figure 3.1.

Substrate selection depends on the application. One of the main drives today is the trend toward flexible substrates. The substrate for electronic devices can be the conventional FR-4 (glass-reinforced epoxy) or polyimide sheets. The substrate can also be a 3D-printed component, for example, antenna or interconnects printed on a 3D-printed electronic package or case. There are few options for printed 3D substrates and one of them is acrylonitrile butadiene

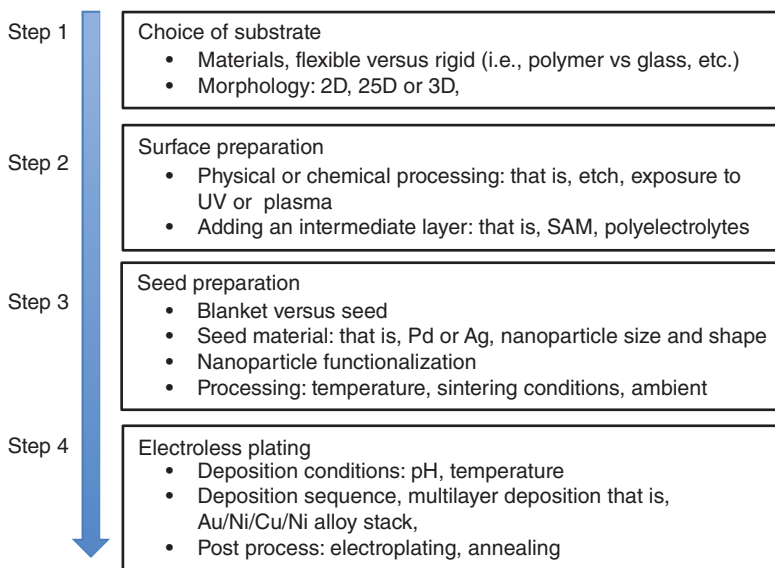


Figure 3.1 Diagram of the problems and decisions sequence in electroless plating on printed seed.

styrene (ABS), which is a very hydrophobic substrate with relatively low working temperatures (typically below 80 °C). Direct printing of Ag ink on ABS “as is” does not produce continuous lines. However, treating the ABS surface with oxygen plasma improves wetting and thus improves the metal seed printing quality. Further improvement is achieved by treating the surface with aminosilanes (such as aminopropyltrimethoxysilane (APTMS) or similar) forming an adhesion promotion layer.

The aminosilane (or similar) surface treatment is also called surface modification and in some cases surface functionalization. The treatment can be either by using chemical or physical methods. It can increase the surface roughness, modify the surface wetting, and modify the surface chemical affinity to the ink, especially to the relevant component of the ink, for example, binding to the metal nanoparticle component of the ink. Adding another interface layer with unique chemical and/or chemical properties is also an option. Ideally, a thin porous interlayer will allow good absorption of the ink while keeping the metal nanoparticle components in place and the liquid phase of the ink is evaporating.

3.4.1 Methods and Approaches

Following the previous analysis, here is an overview of the various approaches for the integration of electroless deposition and printing.

3.4.1.1 Printed Pd Seed

Busato *et al.* [41] reported on the IJP of an aqueous palladium(II) solution onto surface-treated polyimide film, followed by reduction to metallic palladium and electroless copper plating. Using this method, they achieved Cu metal lines with critical dimensions in the range of 100 μm . They described simple Pd ink containing 0.5 mg Pd ml^{-1} . Their ink was reported to be stable for a period of up to 4 months when stored at 4 °C. At room temperature, significant precipitation appeared after 2–3 weeks, thus limiting the applicability of that method. One key feature described in this paper is the surface preparation of the polyimide substrate, which will be discussed later in detail. They found that the process of immersing the film in 10 M potassium hydroxide at room temperature for up to 72 h, rinsing with water, and then drying in air yields a stable Cu deposition on top of the inkjet-printed catalyst. This process causes chemical imide ring opening, surface roughening, and better adhesion of the subsequent layers. The treated surface contact angle (for DI water) was 21–52° compared to 66–74° for the untreated film. Water drops on the treated surface were reported to be stable without lateral spreading. After printing and drying of the palladium(II) ink, no pattern was visible to the naked eye. Short immersion of the printout in 0.1 M sodium borohydride revealed a faint grayish pattern indicating the deposition of metallic palladium. Next, they deposited Cu by electroless plating using a conventional basic (pH = 12.5–12.7) bath at 70 °C. The specific resistivity of deposited Cu was in the range of 3.33–4 $\mu\Omega\text{cm}$, which is about twice that of bulk Cu. Finally, Cu was electroplated to further reduce the line resistance to a desired value. The whole structure was used to build a flexible low-cost active fiber composite (AFC) patch.

3.4.1.2 Printed Ag Ink

Palladium catalysts inks act as a good seed for electroless plating [34–38]. However, reports on their stability indicate limited shelf-life. Therefore, more work is still required to improve their properties rendering them useful for industrial applications. The most common conductive ink today is Ag ink that is widely used for solar cell applications. Few methods have been demonstrated for Ag inkjet printing:

- 1) Silver ink IJP followed by direct deposition of Cu
- 2) Surface coat with special ink containing Ag nanoparticle followed by microplasma printing exposing the Ag nanoparticles [42].

3.4.1.3 Preseed Surface Modification

Cheng *et al.* [16] demonstrated the integration of self-assembled monolayer (SAM) processing with polyelectrolyte multilayers (PEMs) and IJP of a catalyst, followed by electroless plating of metal for large-area metallization on plastics. They deposit Cu from a basic bath with pH ranging from 8.7 to 9.0 using dimethylamine borane (DMAB; reducing agent). The catalyst was Na_2PdCl_4 (5 mM) in DI water. The effective Cu resistivity was about 8 times the bulk value ($1.67 \mu\Omega \text{ cm}$).

3.4.2 Electroless Metal Integration: Examples

As mentioned earlier, there are few options for electroless plating process on printed parts. The easiest and common process is electroless copper plating, mainly due to two reasons: first, low-cost source materials compared to other expensive metals, such as gold or silver. Second, the working conditions of the electroless copper plating process are easier to perform than other electroless processes, for example, the plating bath temperature. Electroless nickel requires high temperature to activate the catalyst, so the nickel bath temperature is $80\text{--}90^\circ\text{C}$. On the contrary, the needed temperature for the electroless copper is only $40\text{--}70^\circ\text{C}$. Another issue is the stability of the bath which requires good control of the concentrations of the different ingredients, mainly the metal ions and the reducing agent. Other electroless solutions such as silver solutions are less stable. The plating reaction begins by initiating the catalyst in the solution, and from this point, the reaction is spontaneous until ending one of the chemical reaction ingredients. This fact limits the stability of these solutions for few hours, and losing its reactivity after this time.

Electroless plating, similar to other plating processes, needs a pretreatment process of the substrate before plating, in order to enable good adhesion between the substrate and the plated layer. Discussing pretreatment process regarding printed parts must be divided into few sections, according to the different types of substrate.

Most of the printing technologies create an object from one or more different types of polymers. The pretreatment process before electroless plating of polymeric surface basically has three stages:

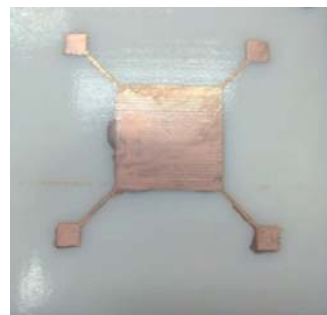
- 1) First metallization – dipping the printed part in different metal ion solutions, for example, solutions with Sn^{+2} ions.
- 2) Changing ions – replacing the Sn^{+2} ions on the surface with Pd^{+2} ions. This change can be achieved by using palladium chloride solutions.
- 3) Reducing reaction – reducing the Pd^{+2} ions, which enable the Cu^{+2} ions to catch on the treated surface.

In the case of using silver ink for printing areas in the object, the result is a combined structure: part of it is polymeric and the other part is semimetallic layer. After the object passes the sintering process, it is changed to polymeric and metallic parts, according to the different areas. Since it already had metallic parts, there is no need for three stages of pretreatment process. The only stage that is needed is the last one. The reducing reaction of the metal layer enables electroless process, which will react only with the printed silver to build a new metallic layer (Figure 3.2).

This process enables the building of metallic layer on the entire surface, changing the electrical property of an object from isolated to conductive. Instead of traditional technologies that involve taking metal raw material and machining it to needed dimensions with the disadvantages of cost and time duration of production, there is a new approach of building using this process. 3D printing of polymer object takes shorter time to produce and changing it to object with electrical properties of metal. Of course, it cannot replace the metal parts in cases when mechanical properties are required, but in cases where the basic demand is for conductivity – this option is an excellent solution.

A significant advantage of this selective process is the option to improve the conductivity of the metallic interconnections. The basic concept is using the printed silver as a seed layer – the basis for building the electrical connections that give electrical abilities. The thickness of the silver after printing and sintering is about 50–200 nm. The electroless copper plated on this seed layer can achieve 2–10 μm . The improvement of the conductivity is significant. The printed silver reaches resistivity in the range of $9 \times 10^{-4} \Omega \text{ cm}$ before sintering and $\sim 3 \times 10^{-6} \Omega \text{ cm}$ after sintering at 300C for 10 min. (on Kapton®) compared to resistivity of $\sim 2 \times 10^{-6} \Omega \text{ cm}$ after copper plating.

Figure 3.2 Copper layer(2 μm thick) built on inkjet-printed silver. The flat substrate is "VeroClear™" by Stratasys Inc. demonstrating 2D object plating.



In general, the metal is being printed only on the outer surface, in order to build electrical connection between different points on the printed object. More interesting is the option to build internal connections inside the printed object. New design of the object, taking into account the metallic layer based on silver printed with electroless plating, can lead to new options for very wide range of applications. The option to use the ability of building electrical connections inside an object in this new approach leads to new opportunities and new thoughts for new design of electrical devices. For example, it can easily be used to improve the Printed Circuit Board (PCB) efficiency, by removing the electrical connections from the surface of the PCB, and building them inside the PCB as internal connections. Just like the change that 3D printing brings to the “short runs” market, the ability of adding electrical properties to these printed objects can change the electrical devices market (Figure 3.3).

In other cases, such as silver printing on PET and PEN, which are useful for simple electrical devices such as antennas or sensors, the plating process can reduce the resistivity to values of $2 \mu\Omega \text{ cm}$ after plating (Figure 3.4).

Another interesting option is to use the printed silver as a basis for other functional layers. One optional application for this process is changing the layer color by adding carbon nanotubes in order to sign something. Another optional application is preventing the oxidation of the printed silver. The printed silver, similarly to other metals, undergoes oxidation process with time. Electroless silver plating on the printed silver, improve the layers conductivity, further prevent the oxidation if additives like tungsten ions are added to the plating solution.

A second example is the IJP on 3D-printed part. In this case, we show here a CuCo alloy that has been deposited on a 3D printed substrate (VeroWhite™). Attempts to print directly on that surface failed due to “dewetting” of the ink. Therefore, the surface was cleaned and treated in oxygen plasma for a short time.



Figure 3.3 3D cone-shaped copper plated layer on 3D silver printed. The copper layer connects the bottom and topside of the cube. The raw material of printed cubic is "VeroClear™" by Stratasys Inc.



Figure 3.4 van der Pauw resistivity measurements printed with Ag nanoparticles on PET, before (left) and after (right) electroless copper plating.

Figure 3.5 Electroless CuCo alloy deposited on inkjet-printed (Dimatix™ DMP-2831) seed on polymer used 3D printing (VeroWhite™ by Stratasys Inc.).



Then, it was treated in a solution of aminopropyltriethoxysilane (APTES). Such surfaces showed good wetting properties allowing stable printing of the Cu alloy (Figure 3.5).

3.5 Summary and Conclusions

Integrating electroless plating with printing has many advantages. It is a pragmatic approach that, if done correctly, will have the following advantages:

- 1) Improve line conductivity by electroless plating.
- 2) Low-temperature process. Electroless plating deposition temperature are typical in the range of up to 90 °C. This range is suitable for many types of substrates. Note that common polymers such as ABS for 3D printing have low glass transition temperature and they show significant warping at temperatures above 60 °C. Deposition on such structures requires plating bath at temperatures below 60 °C, which is possible.
- 3) Faster overall process. Although it involves two tools, the electroless plating process can be done in a “batch” running many samples in parallel while printing is by its nature a serial process.

- 4) Electroless plating may be used as passivation (capping) layer. For example, electroless CoWP or Ni alloys are known to act as barrier layer at temperatures exceeding 400 °C.
- 5) It allows deposition of unique alloys and multilayer structures that are not available for the printing industry.
- 6) It allows the use of an existing technology with large manufacturing base and knowhow.

However, there are also some issues to be considered:

- 1) It is a “two-tool” process that requires special equipment for each process and for the intermediate steps (i.e., cleaning and drying).
- 2) Special metal seed ink may be required. A very thin seed layer is required for electroless plating. There is no need for thick seed layer to initiate the electroless plating process.
- 3) There are adhesion problems at low-temperature processes on polymers. Special surface adhesion promotion steps are required. This includes physical or chemical surface treatment or adding special adhesion promotion layers. The ideal surface for the seed layer should retain the seed material in a confined area, support good adhesion to the surface, and remain stable during the deposition process.
- 4) Electroless metal may now be useful for thick layers, more than few microns. At large thickness, electroless metals, such as electroless copper, may have cracking and delamination problems.

Integrating electroless plating can be used for many applications such as for 3D objects [43], electrode arrays [44], sensors [45], and on wearable devices [46]. Although this list is not exhaustive, more applications are emerging rapidly. In summary, integrating electroless plating with the printing industry is a desirable approach that can and should be adopted for many applications. It still requires further investigation; however, it has already been demonstrated with satisfactory results.

References

- 1 Andricacos, P.C., Uzoh, C., Dukovic, J.O., Horkans, J., and Deligianni, H. (1998) Damascene copper electroplating for chip interconnections. *IBM J. Res. Dev.*, **42** (5), 567–574.
- 2 Calvert, P. (2001) Inkjet printing for materials and devices. *Chem. Mater.*, **13** (10), 3299–3305.
- 3 Mallory, G.O. and Hadju, J.B. (1990) *Electroless Plating Fundamentals and Applications*, American Electroplaters and Surface Finishers Society, International Headquarters, Orlando, Florida.
- 4 Shacham-Diamand, Y., Osaka, T., Okinaka, Y., Sugiyama, A., and Dubin, V. (2015) 30 years of electroless plating for semiconductor and polymer micro-systems. *Microelectron. Eng.*, **132**, 35–45.

- 5 Djokić, S.S. (2002) Electroless deposition of metals and alloys, in *Modern Aspects of Electrochemistry*, No.35 (eds B.E. Conway, R. White, and J.O.' M. Bockris), Kluwer Academic/Plenum Publishers, New York, pp. 51–120.
- 6 Schlesinger, M. and Paunovic, M. (eds) (2010) *Modern Electroplating*, Fifth edn, John Wiley & Sons, Inc..
- 7 Dubin, V.M. *et al.* (2004) Chapter 2: Electroplating process for Cu chip metallization & Chapter 3: Electroless barrier and seed layers for on- chip metallization, in *New Trends in Electrochemical Technology, Microelectronic Packaging* (eds M. Datta, T. Osaka, and J.W. Schultze), CRC Press, New York, p. 3, p. 31.
- 8 Murphy, S.V. and Atala, A. (2014) 3D bioprinting of tissues and organs. *Nat. Biotechnol.*, **32** (8), 773–785.
- 9 Leigh, S.J., Bradley, R.J., Pursell, C.P., Billson, D.R., and Hutchins, D.A. (2012) A simple, low-cost conductive composite material for 3D printing of electronic sensors. *PLoS One*, **7** (11), e49365.
- 10 Hasegawa, M., Negishi, Y., Nakanishi, T., and Osaka, T. (2005) Effects of additives on copper electrodeposition in submicrometer trenches. *J. Electrochem. Soc.*, **152** (4), C221–C228.
- 11 Pourbaix, M. (1966) *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press.
- 12 Ohno, I. (1991) Electrochemistry of electroless plating. *Mater. Sci. Eng., A*, **146**, 33–49.
- 13 Okinaka, Y. and Osaka, T. (2008) Electroless deposition processes: Fundamentals and applications. *Adv. Electrochem. Sci. Eng.*, **2**, 55–116.
- 14 Osaka, T., Okinaka, Y., Sasano, J., and Kato, M. (2006) Development of new electrolytic and electroless gold plating processes for electronics applications. *Sci. Technol. Adv. Mater.*, **7** (5), 425–437.
- 15 Iwu, K.O., Strano, V., Di Mauro, A., Impellizzeri, G., and Mirabella, S. (2015) Enhanced quality, growth kinetics, and photocatalysis of ZnO nanowalls prepared by chemical bath deposition. *Cryst. Growth Des.*, **15** (9), 4206–4212.
- 16 Cheng, K., Yang, M.H., Chiu, W.W.W., Huang, C.Y., Chang, J., Ying, T.F. *et al.* (2005) Ink-jet printing, self-assembled polyelectrolytes, and electroless plating: Low cost fabrication of circuits on a flexible substrate at room temperature. *Macromol. Rapid Commun.*, **26**, 247.
- 17 Liao, Y.C. and Kao, Z.K. (2012) Direct writing patterns for electroless plated copper thin film on plastic substrates. *ACS Appl. Mater. Interfaces*, **4** (10), 5109–5113.
- 18 Aldakov, D., Bonnassieux, Y., Geffroy, B., and Palacin, S. (2009) Selective electroless copper deposition on self-assembled dithiol monolayers. *ACS Applied Materials & Interfaces*, **1** (3), 584–589.
- 19 Moran, C.E., Radloff, C., and Halias, N.J. (2003) Benchtop fabrication of semiconductor metal line and island arrays using passive microcontact printing and electroless plating. *Adv. Mater.*, **15** (10), 804–807.
- 20 Shah, P., Kevrekidis, Y., and Benziger, J. (1999) Ink-jet printing of catalyst patterns for electroless metal deposition pratik shah, yannis kevrekidis, and Jay benziger. *Langmuir*, **15**, 1584–1587.

- 21 Lok, B.K., Liang, Y.N., Gian, P.W., Xuechuan, S. and Lu, A.C.W., *Process Integration of Inkjet Printing and Electroless Plating for LTCC Substrates*, 2007 9th Electronics Packaging Technology Conference
- 22 Subramanian, V., Fréchet, J.M.J., Chang, P.C., Huang, D.C., Lee, J.B., Molesa, S.E., Murphy, A.R., Redinger, D.R. and Volkman, S.K., *Progress Toward Development of All-Printed RFID Tags: Materials, Processes, and Devices*, Proceedings of The IEEE Vol. 93, No. 7, July 2005
- 23 Charbonnier, M., Romand, M., Goepfert, Y., Leonard, D., and Bouadi, M. (2006) Copper metallization of polymers by a palladium-free electroless process. *Surf. Coat. Technol.*, **200**, 5478–5486.
- 24 Garcia, A., Berthelot, T., Viel, P., Mesnage, A., Jegou, P., Nekelson, F., Roussel, S., and Palacin, S. (2010) ABS polymer electroless plating through a one-step poly(acrylic acid) covalent grafting. *ACS Appl. Mater. Interfaces*, **2**, 1177–1183.
- 25 Kranzlin, N., Ellenbroek, S., Duran-Martin, D., and Niederberger, M. (2012) Liquid-phase deposition of freestanding copper foils and supported copper thin films and their structuring into conducting line patterns. *Angew. Chem. Int. Ed.*, **51**, 4743–4746.
- 26 Shukla, S., Seal, S., Rahaman, Z., and Scammon, K. (2002) Electroless copper coating of cenospheres using silver nitrate activator. *Mater. Lett.*, **57**, 151–156; 1996, **12**, 1375–1380..
- 27 (a) Carmichael, T.B., Vella, S.J., and Afzali, A. (2004) Selective electroless metal deposition using microcontact printing of phosphine–phosphonic acid inks. *Langmuir*, **20**, 5593–5598; (b) Basarir, F. (2012) Fabrication of gold patterns via multilayer transfer printing and electroless plating. *ACS Appl. Mater. Interfaces*, **4**, 1324–1329.
- 28 Tseng, C.C., Chang, C.P., Ou, J.L., Sung, Y., and Ger, M.D. (2008) The preparation of metal–styrene oligomer and metal–SSNa nanocomposites through single thermal. *Colloids Surf., A*, **330**, 42.
- 29 Tseng, C.C., Chang, C.P., Ou, J.L., Sung, Y., and Ger, M.D. (2009) Noble metallic nanoparticles reduced by PS-based oligomers through one-step synthesis. *Colloids Surf., A*, **333**, 138.
- 30 Tseng, C.C., Lin, Y.H., Shu, Y.Y., Chen, C.J., and Ger, M.D.J. (2011) Synthesis of vinyl acetate/Pd nanocomposites as activator ink for ink-jet printing technology and electroless copper plating. *J. Taiwan Inst. Chem. Eng.*, **42**, 989–995.
- 31 Zabetakis, D. and Dressick, W.J. (2012) Statistical analysis of plating variable effects on the electrical conductivity of electroless copper patterns on paper. *ACS Appl. Mater. Interfaces*, **4**, 2358–2368.
- 32 Sridhar, A., Reiding, J., Adelaar, H., Achterhoek, F., Dijk, V.D.J., and Akkerman, R. (2009) Inkjetprinting- and electroless-plating- based fabrication of RF circuit structures on high-frequency substrates. *J. Micromech. Microeng.*, **19**, 085020.
- 33 Shah, P., Kevrekidis, Y., and Benziger, J. (1999) Ink-jet printing of catalyst patterns for electroless metal deposition. *Langmuir*, **15**, 1584.
- 34 Kao, C.Y. and Chao, K.S. (2007) Electroless copper plating onto printed lines of nanosized silver seeds. *Electrochem. Solid-State Lett.*, **10**, D32–D34.

- 35 Byeon, J.H. and Roberts, J.T. (2012) Silver deposition on a polymer substrate catalyzed by singly charged monodisperse copper nanoparticles. *ACS Appl. Mater. Interfaces*, **4**, 2515–2520.
- 36 Ghosh, S., Yang, R., Kaumeyer, M., Zorman, C.A., Rowan, S.J., Feng, P.X.-L., and Sankaran, R.M. (2014) Fabrication of electrically conductive metal patterns at the surface of polymer films by microplasma-based direct writing. *ACS Appl. Mater. Interfaces*, **6**, 3099–3104.
- 37 Cauchois, R., Saadaoui, M., Legeleux, J., Malia, T., Dubois-Bonvalot, B., et al.. Chip integration using inkjet-printed silver conductive tracks reinforced by electroless plating for flexible board packages. MiNaPAD 2012. Micro/Nano-Electronics Packaging & Assembly, Design and Manufacturing Forum, Apr 2012, Grenoble, France. pp. F01. <emse-00691806>.
- 38 Suh, S.W., Kim, J.J., Kim, S.H., and Park, B.K. (2012) Effect of PI film surface on printing of Pd(II) catalytic ink for electroless copper plating in the printed electronics. *J. Ind. Eng. Chem.*, **18**, 290–294.
- 39 Ghosh, D.S., Liu, Q., Mantilla-Perez, P., Chen, T.L., Mkhitarian, V., Huang, M., Garner, S., Martorell, J., and Pruneri, V. (2015) Highly flexible transparent electrodes containing ultrathin silver for efficient polymer solar cells. *Adv. Funct. Mater.*, **25** (47), 7309–7316.
- 40 Ghosh, D.S., Chen, T.L., Mkhitarian, V., and Pruneri, V. (2014) Ultrathin transparent conductive polyimide foil embedding silver nanowires. *ACS Appl. Mater. Interfaces*, **6** (23), 20943–20948.
- 41 Busato, S., Belloli, A., and Ermanni, P. (2007) Inkjet printing of palladium catalyst patterns on polyimide film for electroless copper plating. *Sens. Actuators, B*, **123** (2), 840–846.
- 42 Ghosh, S., Yang, R., Kaumeyer, M., Zorman, C.A., Rowan, S.J., Feng, P.X.L., and Sankaran, R.M. (2014) Fabrication of electrically conductive metal patterns at the surface of polymer films by microplasma-based direct writing. *ACS Appl. Mater. Interfaces*, **6** (5), 3099–3104.
- 43 Wang, X., Guo, Q., Cai, X., Zhou, S., Kobe, B., and Yang, J. (2014) Initiator-integrated 3D printing enables the formation of complex metallic architectures. *ACS Appl. Mater. Interfaces*, **6**, 2583–2587.
- 44 Tseng, C.-C., Chou, Y.-H., Hsieh, T.-W., Wang, M.-W., Shu, Y.-Y., and Ger, M.-D. (2012) Interdigitated electrode fabricated by integration of ink-jet printing with electroless plating and its application in gas sensor. *Colloids Surf., A*, **402**, 45–52.
- 45 Sawhney, A., Agrawal, A., Lo, T., Patra, P.K., Chen, C.H., and Calvert, P. (2007) Soft-structured sensors and connectors by inkjet printing. *AATCC Rev.*, **7** (6), 1–10.
- 46 Calvert, P., Duggal, D., Patra, P., Agrawal, A., and Sawhney, A. (2008) Conducting polymer and conducting composite strain sensors on textiles. *Mol. Cryst. Liq. Cryst.*, **484** (1), 291/[657]–302/[668]. doi: 10.1080/15421400801904690

4

Reactive Inkjet Printing as a Tool for *in situ* Synthesis of Self-Assembled Nanoparticles

Ghassan Jabbour, Mutalifu Abulikamu, Hyung W. Choi, and Hanna Haverinen

4.1 Introduction to Reactive Inkjet Printing

Passive and functional materials and devices fabricated in part or whole using printing techniques, including screen printing, gravure printing, transfer printing, and inkjet printing (IJP), have been the subjects of increasing attention among research and industrial avenues alike [1–9]. The ultimate drive behind such interests is mainly the reduction in cost of manufacturing and the potential to fabricate devices on any substrate including traditional silicon, glass, and nontraditional ones such as textile, flexible plastic, and paper, to mention a few. Among such approaches, thermal or piezoelectric IJP has been used for many years in materials and device research as a tool to deposit, and/or pattern, preformulated passive inks made up of given materials hosted in a liquid to yield a solution (or mixture, or colloidal suspension, etc.) of certain viscosity, compatible with the specifications of the inkjet system in question [10]. Polymers, small molecules, colloidal nanoparticles and quantum dots, and biomaterials, to mention a few, have been used in an inkjet to fabricate certain devices for applications ranging from displays, organic transistors, memory elements, solar cells, sensors, to biomaterials and self-healing polymers [11–20].

In recent years, inkjet has been shown to be a valuable research tool for the modification of physical or chemical properties of materials and/or synthesis of materials on various scales [18, 21–26]. Thus, the term reactive inkjet (RIJ) printing (RIP) is used in such cases [24]. In the RIJ approach, the inks are no longer passive, but they can be reactive or combination of passive and reactive – depending on the needs of the process at hand. Since the disposed amounts are minute (picoliters), RIJ provides an environmentally conscious alternative to traditional chemical synthesis. Moreover, the on-demand ability to place, and pattern if needed, various chemicals with great and repeatable accuracy renders RIJ as a useful tool in combinatorial and rapid screening discovery of materials and devices [21, 22].

RIJ was introduced in the area of organic electronics as a chemical patterning approach to allow for highly controlled modification of the sheet resistivity of conductive polymer electrodes [21]. Recently, Jabbour *et al.* demonstrated the preparation of self-assembled nanoparticles via RIJ approach [27, 28]. Such an application opens up new avenues in materials and device engineering. In this

chapter, we discuss such approaches and the recent advances in regard to the significant reduction in processing time. The approach has been used to synthesize various metals, alloys, and non-metal-based nanoparticles. However, due to limitation of space, we restrict our discussion to RIJ formation of gold nanoparticles (Au NPs).

Au NPs hold great promise in several technological areas including, but not limited to, forensics [29], electrochemical sensing [30], biology [31], energy [32–36], and photonics [37, 38], to mention a few. Some of the attributes that make Au NPs more attractive to use over its metallic counterparts (e.g., aluminum, copper) include at least one of the following characteristics: (i) nontoxicity (in today's understanding), (ii) fast response to external electric and magnetic fields, (iii) stability, and (iv) relative ease of its synthesis, to mention a few.

Au NPs can be synthesized using high vacuum deposition techniques including thermal evaporation or sputtering [39, 40], lithography [41–43], and others. However, such techniques are either slow or result in nonuniform particle size distribution, or are expensive and time consuming. The overwhelming majority of recent approaches to the synthesis of Au NPs rely on wet chemical methods [44–46]. In most cases, once synthesized, the Au NPs are purified, followed by a step to stabilize them – by functionalizing their surfaces with certain ligands – to render them dispersible in a given organic liquid. The resulting colloidal system can be then used in several deposition approaches including spin coating, spraying, IJP, and others. The attractiveness of IJP of Au NPs lies in several features including real-time deposition and patterning, on-demand deposition at any place over the substrate surface, accurate control of droplets volume, and efficient use of materials (e.g., compared to spin coating or screen printing), and so on. The combined two-step process – syntheses of the Au NPs ink and its consequent use in IJP – is rather cumbersome and time consuming. Moreover, it is not possible to use the Au NP colloidal ink to infiltrate porous material, or membrane, having an average pore diameter smaller than that of the Au NPs. A solution to this can come from the utilization of RIJ process as an *in situ* synthesis and patterning tool of self-assembled Au NPs [27, 28]. Such an approach is amenable to low-cost manufacturing of nanomaterials and can be applied not only to metal nanoparticle synthesis but also to other nanomaterials composed of inorganics, organics, or hybrids. In the following sections, we limit our discussion to the demonstration of *in situ* self-assembled syntheses of Au NPs [27, 28] and highlight some of the recent advances in making the process faster and more suitable to near-future adoption by industry.

4.2 RIJ of Self-Assembled Au NPs

In what follows, the inkjet used was Dimatix Materials Printer DMP-2800 with cartridge having a 22 μm nozzle diameter capable of dispensing 10 pl droplet volume. The printhead has a single line of 16 nozzles having 254 μm spacing. Due to the relatively low viscosity of the inks used, the nozzles' driving voltage was

tuned to the range of 6–9 V. Unless otherwise specified, the substrate-to-nozzle distance was about 0.25 mm. All printing steps occurred in air, with the substrate maintained at room temperature. The Si substrates were precleaned with an ultrasonic bath of deionized water, followed by 10 min baths in acetone, ethanol, and isopropanol, respectively. The substrates were dried immediately after each sonication step, using nitrogen gas. Plasma ashing of the cleaned substrates was carried out prior to commencing inkjet deposition (printing) step. Although in the experiments described here we used silicon (100), similar results were obtained on substrates other than silicon [27].

Two cartridges were used in sequence, with one (cartridge A) containing a 10 ml : 1 ml mixture of 1,2-dichlorobenzene (dispersion solvent) and oleylamine (reducing and capping agent) and the second (cartridge B) containing 0.12 mmol of gold(III) chloride hydrate $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (gold precursor) in 10 ml of dimethyl sulfoxide (DMSO). The surface tension of ink A and its contact angle with Si-wafer surface were measured to be 29.68 mN m^{-1} and 28.60° , respectively. Droplets from second printing step B were positioned exactly on top of those dispensed from cartridge A, as shown in the experimental scheme of Figure 4.1. The surface tension and contact angle of ink B were 43.88 mN m^{-1} and 35.75° , respectively [27]. The surface tension was measured at 22.6°C using Kruss Tensiometer (K100MK2/SF/C). The contact angle was measured at room temperature (about $22\text{--}23^\circ\text{C}$) using Kruss EasyDrop. The choice of DMSO and 1,2-dichlorobenzene as solvents was driven by their suitable viscosity and surface tension, and relatively higher boiling point. Moreover, the acceptable solubility of the gold precursor in DMSO results in the formation of stable ink and allows for high-concentration solutions to be formulated. Many factors affect the growth of uniform NPs, which include, but not limited to, mixing

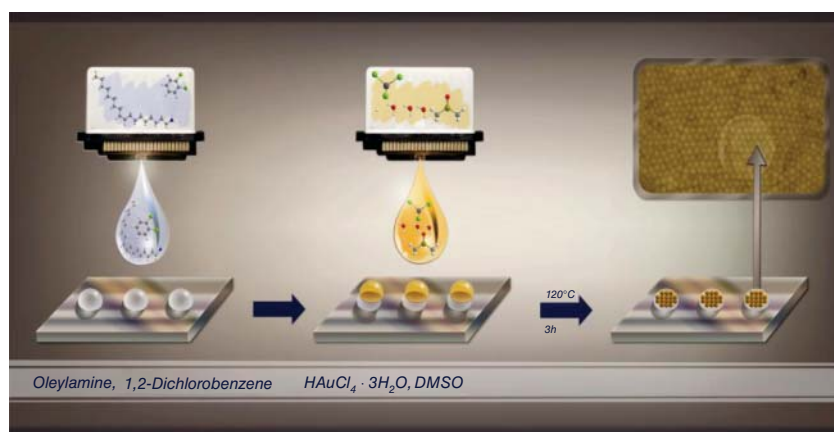


Figure 4.1 RIJ printing scheme resulting in self-assembled Au NPs. Ink A (left) is printed first, followed by printing of ink B (middle) on top of A. Printing was carried out in air at room temperature. The substrate was then heated to 120°C to result in Au NP array (right). The right-side image is an actual high-resolution SEM scan shown in Figure 4.3. (Abulikemu *et al.* (2014) [27]. Reproduced with permission of Wiley.)

uniformity of the components of ink A and those of ink B and the uniform mixing of A and B once printed upon the substrate. In this regard, the coverage of ink B over the area of printed ink A should be near complete to allow rapid and uniform mixing of the two inks over the substrate surface. DMSO and 1,2-dichlorobenzene are relatively miscible, thus mitigating the shortcoming of the relative immiscibility of oleylamine in DMSO.

Following the printing scheme shown in Figure 4.1, a square array of 30- μm -spaced drops was printed on the substrate (Figure 4.2). Once the printing process was finished, the substrate was immediately heat treated for 3 h at 120 °C. The experiment was carried out several times, and representative data are presented here.

The samples were cooled and then placed inside a high-resolution SEM (HRSEM-Nova NANO 600). Figure 4.3 is an HRSEM image revealing the self-assembly of nanoparticles with an average diameter of about 8 ± 2 nm, within each of the printed areas shown in Figure 4.2. As seen in Figure 4.3, the nanoparticles are densely packed having relatively uniform spacing between them.

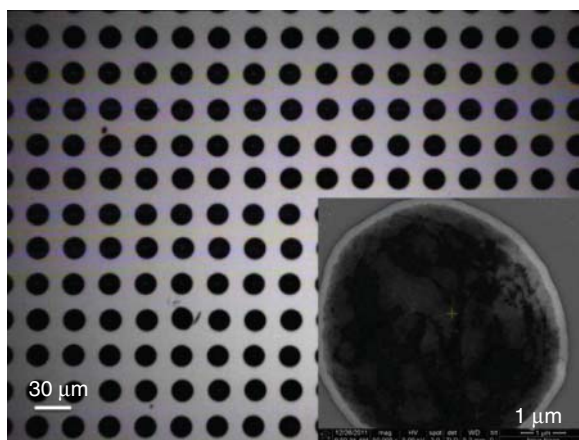


Figure 4.2 Printed square array of droplets of ink B on top of ink A, according to scheme of Figure 4.1. A 30 μm spacing between drops (center-to-center) was used. Inset is a SEM image of an array spot after heat treatment. Note the shrinkage in diameter of the spot. (Abulikemu *et al.* (2014) [27]. Reproduced with permission of Wiley.)

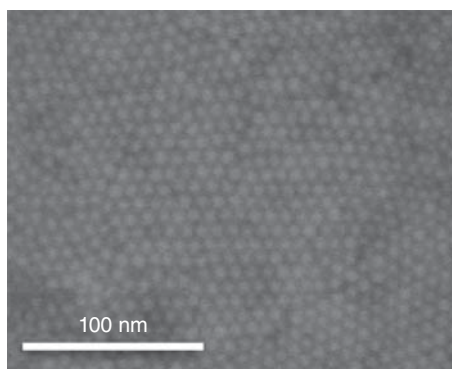


Figure 4.3 HRSEM of printed areas after the heat treatment. The average diameter of the NPs is about 8 ± 2 nm. (Abulikemu *et al.* (2014) [27]. Reproduced with permission of Wiley.)

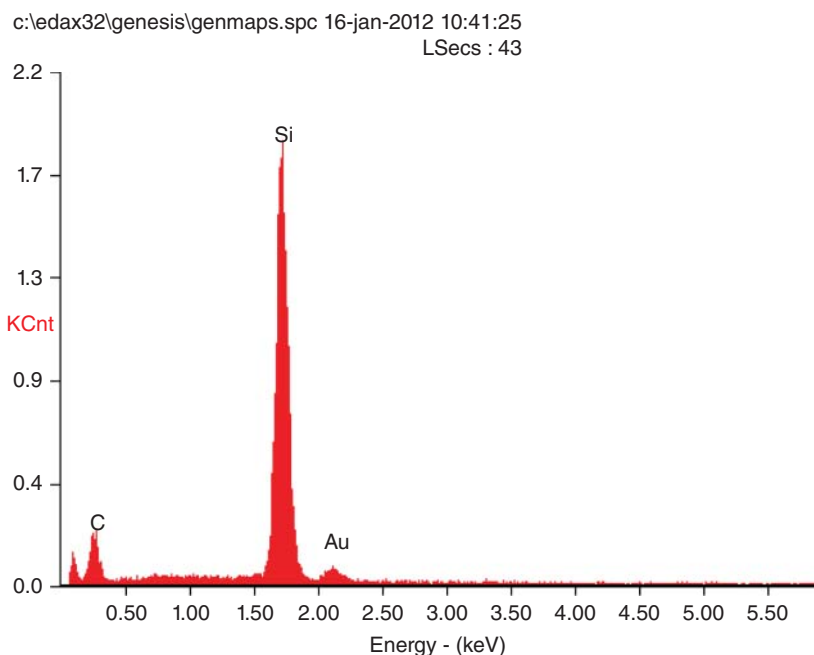


Figure 4.4 Post-heat-treatment EDS analysis of the printed features. The dominating Si peak is due to the silicon substrate. (Abulikemu *et al.* (2014) [27]. Reproduced with permission of Wiley.)

Energy-dispersive X-ray spectroscopy (EDS) of the nanoparticles indicated the presence of gold and carbon, dominated by a silicon signal originating from the substrate, as shown in Figure 4.4. In this case, the source of carbon is the oleylamine capping ligands on the surface of the Au NPs, which is also responsible for the apparent uniform spacing between adjacent NPs.

The crystal structure of the Au NPs was confirmed using Bruker D8 Discover high-resolution X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM-Titan ST 300 kV by FEI). For cross-sectional TEM analysis, a focused ion beam (Helios 400s by FEI) with lift-out method was used. Ga ion beam (30 kV, 0.28 nA) was used to thin down the lamellar. The resulting sample was cleaned at 2 kV and 47 pA. The respective results of the two studies are shown in Figure 4.5. In this case, the nanoparticles showed a crystalline Au structure as apparent from XRD (Figure 4.5a), supported by the electron diffraction peaks in the inset of the HRTEM image (Figure 4.5b). The lattice spacing measured by HRTEM were 2.35 and 2.03 Å corresponding to planes (111) and (002) of face-centered cubic (fcc) structure of gold, respectively [47, 48], which also agrees well with the spacing calculations using the XRD results.

It is possible to grow Au NPs using the reverse printing steps. In this case, ink B shown in Figure 4.1 was printed first followed by ink A. The silicon substrates with the printed pattern were then heat treated. In this case, a typical SEM image (Figure 4.6) reveals the formation of Au NPs. However, the size distribution is relatively nonuniform compared to that of Au NPs shown in Figure 4.3, which were

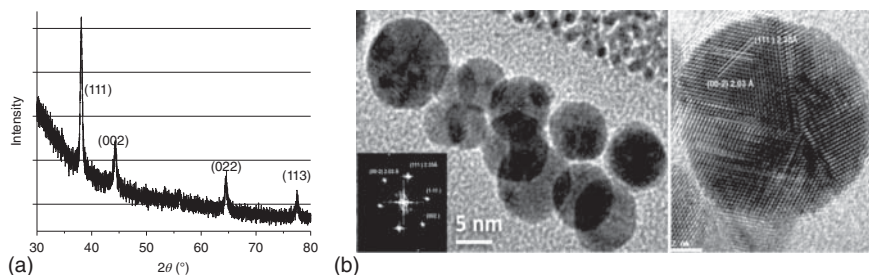


Figure 4.5 XRD (a) and HRTEM (b) images of Au NPs grown by RIJ printing as described in Figure 4.1. Electron diffraction pattern shown in the inset of (b) agrees well with the FCC structure indicated by the XRD results. (Abulikemu *et al.* (2014) [27]. Reproduced with permission of Wiley.)

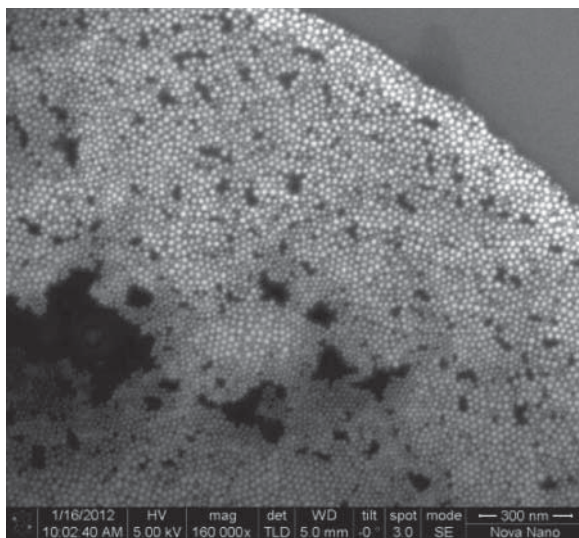


Figure 4.6 Au NPs obtained using a reverse printing scheme to that shown in Figure 4.1.

obtained using the printing sequence of ink A first followed by ink B (Figure 4.1). A detailed study to understand the causes behind this observation is underway.

4.3 Parameters Influencing the Growth of Au NPs

In the liquid phase, several parameters affect the growth of metal nanoparticles including, but not limited to, solvent, concentration of various components, precursor used, temperature and time, printing conditions, and sequence, to mention a few. Here, we limit our discussion to few examples. In this regard, we document the impact of three solvent systems: (i) gold precursor in water (ink A) and oleylamine in ethanol (ink B), (ii) gold precursor in a mixture of ethanol/toluene (1/10) and oleylamine in toluene, and (iii) gold precursor in dimethylformamide (DMF) and oleylamine in toluene. Figure 4.7 shows the SEM images of Au NPs formed from the printed materials using the three different

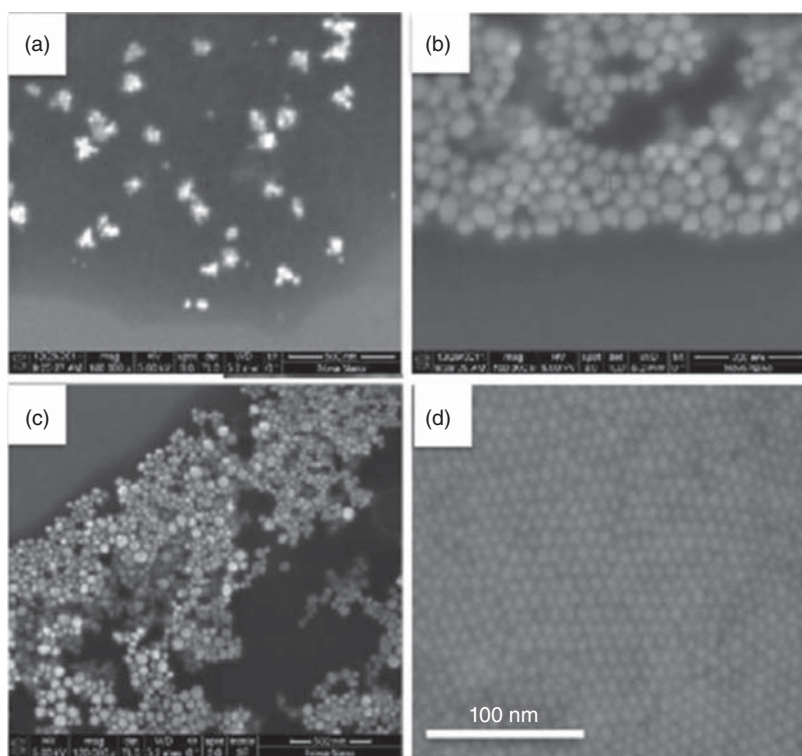


Figure 4.7 Au NPs grown using two inks for each printing experiment made of (a) gold precursor in water and oleylamine in ethanol, (b) gold precursor in a mixture of ethanol/toluene (1/10) and oleylamine in toluene, (c) gold precursor in DMF and oleylamine in toluene, and (d) 10 ml:1 ml mixture of 1,2-dichlorobenzene and oleylamine (ink A) and gold precursor in DMSO (ink B). Scale bar: (a) 500 nm, (b) 200 nm, (c) 500 nm, and (d) 100 nm.

inks mentioned earlier. The scheme of Figure 4.1 was used to print the inks, followed by heat treatment to produce the Au NPs. Au NPs obtained from an ink based on gold precursor in water and oleylamine in ethanol are shown in Figure 4.7a. Nanoparticles obtained from using printed ink of gold precursor in a mixture of ethanol/toluene, followed by printing the ink made of oleylamine in toluene, is shown in Figure 4.7b. Figure 4.7c represents the SEM image of Au NPs resulting from the use of ink consisting of mixture of gold precursor in DMF, and the second step ink of oleylamine in toluene. The SEM image of Au NPs resulting from the solvent system consisting of gold precursor in DMSO and oleylamine in dichlorobenzene (Figure 4.3) is reproduced in Figure 4.7d for comparison. It is clear that the three solvent systems mentioned earlier result in Au NPs having a wide range of sizes and nonuniform coverage of the substrate surface (Figure 4.7a–c). In this case, the higher surface tension of water and lower boiling point of toluene and ethanol are some of the underlying causes of the observed growth of Au NPs. In this particular example, Figure 4.7d represents the most favored inks and printing sequence to grow Au NPs with good size uniformity.

Upon increasing the gold precursor concentration from 0.12 mmol (Figures 4.1 and 4.7d) to 0.4 mmol in DMSO, a noticeable change in the shape of the grown Au NPs was observed [49, 50], as indicated in Figure 4.8. Relatively uniform Au NPs can be grown with an average size of about 25 nm (Figure 4.9) when the concentration of gold precursor and oleylamine is increased to 2 mmol of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 ml of DMSO and 3 ml of oleylamine in 10 ml of 1,2-dichlorobenzene, respectively.

When AuCl_3 was used as gold precursor instead of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, while using all other components of the printing process shown in Figure 4.1, the same relatively broad distribution of Au NPs was obtained after 3 h of heat treatment at 120 °C.

Figure 4.10 shows the SEM image of the formed Au NPs. As can be seen, the NPs have nonuniform size across the printed area, as opposed to the relatively uniform Au NPs obtained when $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was used (Figure 4.3). Further

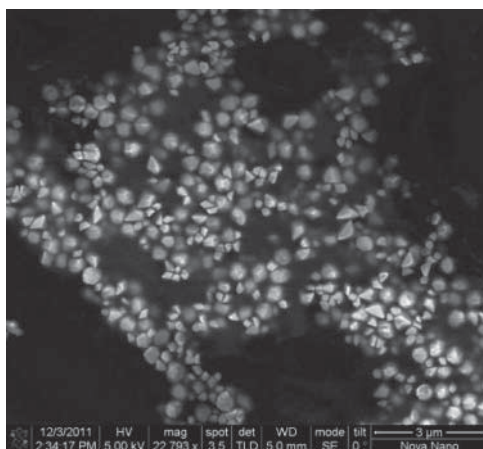


Figure 4.8 SEM image of Au NPs formed using the solvent system consisting of gold precursor in DMSO and oleylamine in 1,2-dichlorobenzene (Figure 4.3) with gold precursor concentration increased to 0.4 mmol.

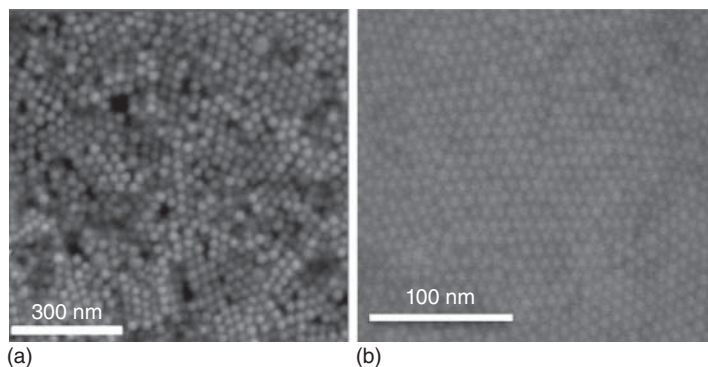
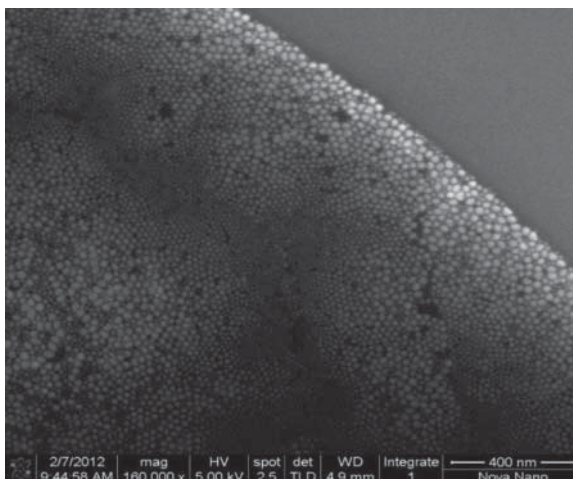


Figure 4.9 SEM image of Au NPs obtained after 3 h heat treatment of printed inks (A and B) at 120 °C. In this case, 2 mmol $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 ml of DMSO and 3 ml of oleylamine in 10 ml of 1,2-dichlorobenzene were used. The figure (b) is inks A and B shown in Figure 4.1. Scale bar: 300 nm (a) and 100 nm (b).

Figure 4.10 SEM image of Au NPs grown using AuCl_3 as the metal precursor instead of $\text{AuCl}_4 \cdot 3\text{H}_2\text{O}$. Scale bar: 400 nm. Note the relatively broad size distribution compared to Figure 4.3.



mapping of various concentrations of AuCl_3 gold precursor is needed to assert whether it is a proper precursor for obtaining uniform Au NPs in RIJ printing.

4.4 Simplifying the Approach (Single Cartridge) Using Single Cartridge Step

It will be advantageous to speed up the synthesis process through simplification of the printing steps involved, thus reducing the overall cost of manufacturing of NPs. In this regard, we investigated the use of single cartridge in the *in situ* self-assembly fabrication of Au NPs. It is worth mentioning that the single ink in this approach does not have longer shelf life compared to the separate component inks of those shown in Figure 4.1.

A single ink mixture was prepared by vigorous stirring of 0.18 mmol of the gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in 10 ml of oleylamine, at room temperature, until a clear solution was obtained.

The resulting solution was passed through a $0.45 \mu\text{m}$ filter prior to its introduction into the inkjet cartridge for immediate printing onto precleaned silicon substrate. In this case, the substrate was kept at 60°C during printing. Upon completing the single-step printing process, the substrates were placed in an oven at 120°C for 2 h. SEM imaging revealed the formation of nearly monodisperse Au NPs (Figure 4.11), with an average diameter of about 22 nm.

4.5 Further Progress toward Reduction of Fabrication Time (1 min)

Several research efforts have been carried out to reduce the synthesis time of Au NPs. Such a reduction in time, along with the use of single ink component prepared immediately prior to the printing process, will have significant

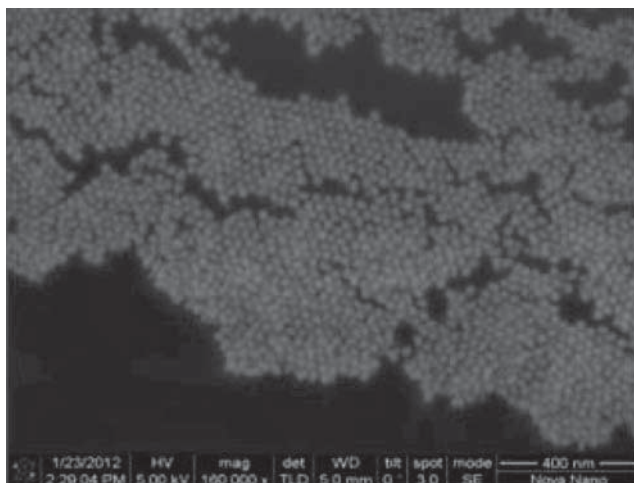


Figure 4.11 SEM image of Au NPs formed upon the use of single cartridge containing 400 nm a single ink mixture of 0.18 mmol of the gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in 10 ml of oleylamine, at room temperature. Scale bar is 400 nm.

impact on the manufacturing process of NPs and in turn on the prices of the NPs. At the time of writing this chapter, 1 ml of water-based dispersion of methyl-terminated, PEG5000-coated Au nanoparticles with an average diameter of 15 nm cost about \$467.50 [Sigma-Aldrich <http://www.sigmaaldrich.com>]. The formation of Au NPs in less than 2 min has been reported using several approaches including (i) NaOH as initiator of PVP reduction of AuCl_4^- [51] and (ii) CO gas as reducing agent [52].

In order to expedite the RIJ synthesis of self-assembled Au NPs, we utilized a rapid photonic heat source (Adphos, NIR42-125) positioned in proximity to the printing process. Using this setup, we were able to synthesize relatively uniform Au NPs in less than 1 min. In this case, the inks used consisted of 1 ml oleylamine in 10 ml chloroform (ink A) and 0.1 mM of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 ml of DMSO (ink B). Ink A was printed first, followed by the printing of ink B on top of A. Three printing schemes were carried out to optimize the surface coverage of the resulting Au NPs: (i) 1 printed drop of ink A followed by 1 drop of ink B, (ii) 1 printed drop of ink A followed by 2 drops of ink B, and (iii) 1 printed drop of ink A followed by 3 drops of ink B. In all three cases, printing of ink B occurred exactly on top of ink A, within the placement accuracy of the printer. As expected, the overall diameter of the printed area increased upon further addition of ink B on top of A. In this case, the diameter of the printed area increased from 30 μm (i) to about 50 μm (iii). Once the printing steps were finished, the samples were immediately exposed to rapid heat-soaking at 170 $^{\circ}\text{C}$ ($\pm 10^{\circ}\text{C}$) for about 1 min. The resulting dried prints were inspected with SEM. Figure 4.12 indicates that a 1 : 3 droplet ratio (ink A:ink B) results in Au NPs having a substrate surface coverage of nearly 100%.

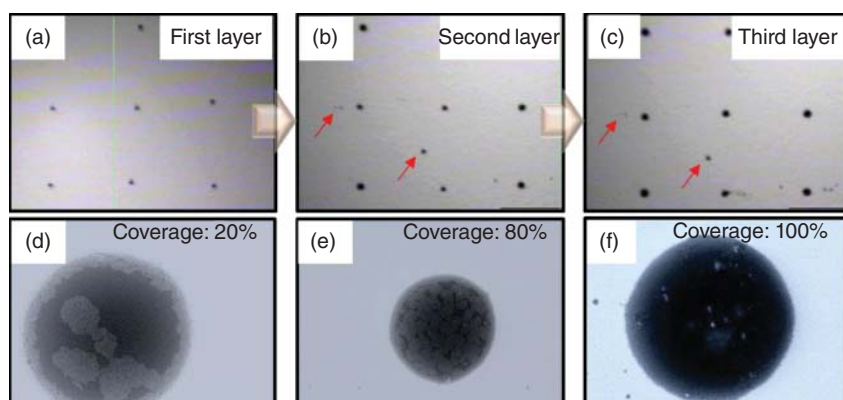


Figure 4.12 (a–c) The printed array before heat treatment. (d–f) SEM images of printed drops upon photonic heat treatment. Image (e) indicates that an 80% surface coverage of Au NPs can already be obtained with 1 printed drop of ink A followed by 2 drops of ink B. A complete surface coverage is obtained using 1 printed drop of ink A followed by 3 drops of ink B as shown in (f).

4.6 Conclusion

In conclusion, RIP can be a valuable tool in the synthesis of nanoparticles. With such a technique, it is possible for simultaneous *in situ* fabrication and patterning of NPs with controlled diameter. This potential approach will find use in many applications ranging from photonics, electronics, biomedical, and smart textile, to mention a few. Reducing the steps and growth time, as shown here, will certainly have a positive impact on the price of the NPs. Although we have focused our attention in this chapter on Au NPs, the approach has been extended to the synthesis of nanoparticles of various metals, alloys, and nonmetals.

References

- 1 Jabbour, G.E., Radspinner, R., and Peyghambarian, N. (2001) Screen printing for the fabrication of organic light-emitting devices. *IEEE J. Sel. Top. Quantum Electron.*, **7**, 769–773.
- 2 Shaheen, S.E., Radspinner, R., Peyghambarian, N., and Jabbour, G.E. (2001) Fabrication of bulk heterojunction plastic solar cells by screen printing. *Appl. Phys. Lett.*, **79**, 2996–2998.
- 3 Berggren, M., Nilsson, D., and Robinson, N.D. (2007) Organic materials for printed electronics. *Nat. Mater.*, **6**, 3–5.
- 4 Kopola, P., Aernouts, T., Sliz, R., Guillerez, S., Ylikunnari, M., Cheyns, D., Välimäki, M., Tuomikoski, M., Hast, J., Jabbour, G., Myllylä, R., and Maaninen, A. (2011) Gravure printed flexible organic photovoltaic modules. *Sol. Energy Mater. Sol. Cells*, **95**, 1344–1347.

- 5 Søndergaard, R., Hösel, M., Angmo, D., Larsen-Olsen, T.T., and Krebs, F.C. (2012) Roll-to-roll fabrication of polymer solar cells. *Mater. Today*, **15**, 36–49.
- 6 Carlson, A., Bowen, A.M., Huang, Y., Nuzzo, R.G., and Rogers, J.A. (2012) Transfer printing techniques for materials assembly and micro/nanodevice fabrication. *Adv. Mater.*, **24**, 5284–5318.
- 7 Kamysbny, A. and Magdassi, S. (2014) Conductive nanomaterials for printed electronics. *Small*, **10**, 3515–3535.
- 8 Choi, H.W., Zhou, T., Singh, M., and Jabbour, G.E. (2015) Recent developments and directions in printed nanomaterials. *Nanoscale*, **7**, 3338–3355.
- 9 Deol, R.S., Choi, H.W., Singh, M., and Jabbour, G.E. (2015) Printable displays and light sources for sensor applications: A review. *IEEE Sens. J.*, **15**, 3186–3195.
- 10 Magdassi, S. (2010) *The Chemistry of Inkjet Inks*, World Scientific Publishing Company. ISBN: ISBN: 978-981-281-821-8
- 11 Bharathan, J. and Yang, Y. (1998) Polymer electroluminescent devices processed by inkjet printing: I. Polymer light-emitting logo. *Appl. Phys. Lett.*, **72**, 2660–2662.
- 12 Hebner, T.R., Wu, C.C., Marcy, D., Lu, M.H., and Sturm, J.C. (1998) Ink-jet printing of doped polymers for organic light emitting devices. *Appl. Phys. Lett.*, **72**, 519–521.
- 13 Sirringhaus, H., Kawase, T., Friend, R.H., Shimoda, T., Inbasekaran, M., Wu, W., and Woo, E.P. (2000) High-resolution inkjet printing of all-polymer transistor circuits. *Science*, **290**, 2123–2126.
- 14 Yoshioka, Y., Jabbour, G. E. and Calvert, P. (2002) *Inkjet printing of materials as a mimic of biological growth*, International Conference on Digital Printing Technologies, 223–226.
- 15 Calvert, P., Yoshioka, Y., and Jabbour, G.E. (2005) *Inkjet Printing for Biomimetic and Biomedical Materials*, pp. 169–180, Kluwer Academic Publishers. ISBN: ISBN: 978-1-4020-2647-8
- 16 Kamysbny, A., Ben-Moshe, M., Aviezer, S., and Magdassi, S. (2005) Ink-jet printing of metallic nanoparticles and microemulsions. *Macromol. Rapid Commun.*, **26**, 281–288.
- 17 Hoth, C.N., Schilinsky, P., Choulis, S.A., and Brabec, C.J. (2008) Printing highly efficient organic solar cells. *Nano Lett.*, **8**, 2806–2813.
- 18 Singh, M., Haverinen, H., Dhagat, P., and Jabbour, G.E. (2010) Progress in inkjet printing of materials in electronics. *Adv. Mater.*, **22**, 673–685.
- 19 Lien, D., Kao, Z., Huang, T., Liao, Y., Lee, S., and He, J. (2014) All-printed paper memory. *ACS Nano*, **8**, 7613–7619.
- 20 Fleet, E.J., Zhang, Y., Hayes, S.A., and Smith, P.J. (2015) Inkjet printing of self-healing polymers for enhanced composite interlaminar properties. *J. Mater. Chem. A*, **3**, 2283–2293.
- 21 Yoshioka, Y., Calvert, P., and Jabbour, G.E. (2005) Simple modification of sheet resistivity of conducting polymeric anodes via combinatorial ink-jet techniques. *Macromol. Rapid Commun.*, **26**, 238–246.
- 22 Yoshioka, Y. and Jabbour, G.E. (2006) Inkjet printing of oxidants for patterning of nanothick conducting polymer electrodes. *Adv. Mater.*, **18**, 1307–1312.

- 23 Kröber, P., Delaney, J.T., Perelaer, J., and Schubert, U.S. (2009) Reactive inkjet printing of polyurethanes. *J. Mater. Chem.*, **19**, 5234–5238.
- 24 Smith, P.J. and Morrin, A. (2012) Reactive inkjet printing. *J. Mater. Chem.*, **22**, 10965–10970.
- 25 Janoschka, T., Teichler, A., Häupler, B., Jähnert, T., Hager, M.D., and Schubert, U.S. (2013) Reactive inkjet printing of cathodes for organic radical batteries. *Adv. Energy Mater.*, **3**, 1025–1028.
- 26 Jeon, S., Park, S., Nam, J., Kang, Y., and Kim, J. (2016) Creating patterned conjugated polymer images using water-compatible reactive inkjet printing. *ACS App. Mater. Interfaces*, **8**, 1813–1818.
- 27 Abulikemu, M., Daas, E., Haverinen, H., and Jabbour, G.E. (2014) In situ synthesis of Au nanoparticles using reactive inkjet printing. *Angew. Chem. Int. Ed.*, **53**, 420–423.
- 28 Abulikemu, M. and Jabbour, G.E. (2014) In situ synthesis of nanoparticles on substrates by inkjet printing, US Patent 8916457.
- 29 Hussain, I., Hussain, S.Z., Rehman, H.U., Ihsan, A., Rehman, A., Khalid, Z.M., Brust, M., and Cooper, A.I. (2010) In situ growth of gold nanoparticles on latent fingerprints—from forensic applications to inkjet printed nanoparticle patterns. *Nanoscale*, **2**, 2575–2578.
- 30 Jensen, G.C., Krause, C.E., Sotzing, G.A., and Rusling, J.F. (2011) Inkjet-printed gold nanoparticle electrochemical arrays on plastic. Application to immunodetection of a cancer biomarker protein. *Phys. Chem. Chem. Phys.*, **13**, 4888–4894.
- 31 Dykman, L. and Khlebtsov, N. (2012) Gold nanoparticles in biomedical applications: Recent advances and perspectives. *Chem. Soc. Rev.*, **41**, 2256–2282.
- 32 Atwater, H.A. and Polman, A. (2010) Plasmonics for improved photovoltaic devices. *Nat. Mater.*, **9**, 205–213.
- 33 Chen, Y. (2011) Gold nanoparticles for applications in energy and environment: Synthesis and characterization. *Rare Met.*, **30**, 116–120.
- 34 Notarianni, M., Vernon, K., Chou, A., Aljada, M., Liu, J., and Motta, N. (2014) Plasmonic effect of gold nanoparticles in organic solar cells. *Sol. Energy*, **106**, 23–37.
- 35 Oliveira, M.C., Fraga, A.L.S., Thesing, A., Andrade, R.L., Santos, J.F.L., and Santos, M.J.L. (2015) Interface dependent plasmon induced enhancement in dye-sensitized solar cells using gold nanoparticles. *J. Nanomater.*, **2015**, 1–9.
- 36 Yao, M., Jia, X., Liu, Y., Guo, W., Shen, L., and Ruan, S. (2015) Surface plasmon resonance enhanced polymer solar cells by thermally evaporating Au into buffer layer. *ACS Appl. Mater. Interfaces*, **7**, 18866–18871.
- 37 Maier, S.A., Kik, P.G., and Atwater, H.A. (2003) Optical pulse propagation in metal nanoparticle chain waveguides. *Phys. Rev. B*, **67**, 205402-1–205402-5.
- 38 Grubisic, A., Mukherjee, S., Halas, N., and Nesbitt, D.J. (2013) Anomalously strong electric near-field enhancements at defect sites on Au nanoshells observed by ultrafast scanning photoemission imaging microscopy. *J. Phys. Chem. C*, **117**, 22545–22559.
- 39 Tour, J.M., Cheng, L., Nackashi, D.P., Yao, Y., Flatt, A.K., Angelo, S.K.S., Mallouk, T.E., and Franzon, P.D. (2003) Nanocell electronic memories. *J. Am. Chem. Soc.*, **125**, 13279–13283.

- 40 Meriaudeau, F., Downey, T.R., Passian, A., Wig, A., and Ferrell, T.L. (1998) Environment effects on surface-plasmon spectra in gold-island films potential for sensing applications. *Appl. Opt.*, **37**, 8030–8037.
- 41 Tan, B.J.Y., Sow, C.H., Koh, T.S., Chin, K.C., Wee, A.T.S., and Ong, C.K. (2005) Fabrication of size-tunable gold nanoparticles array with nanosphere lithography, reactive ion etching, and thermal annealing. *J. Phys. Chem. B*, **109**, 11100–11109.
- 42 Corbierre, M.K., Beerens, J., and Lennox, R.B. (2005) Gold nanoparticles generated by electron beam lithography of gold(I)–thiolate thin films. *Chem. Mater.*, **17**, 5774–5779.
- 43 Hung, A.M., Micheel, C.M., Bozano, L.D., Osterbur, L.W., Wallraff, G.M., and Cha, J.N. (2010) Large-area spatially ordered arrays of gold nanoparticles directed by lithographically confined DNA origami. *Nat. Nanotechnol.*, **5**, 121–126.
- 44 Turkevich, J., Stevenson, P.C., and Hillier, J. (1951) A study of the nucleation and growth processes in the synthesis of colloidal gold. *Discuss. Faraday Soc.*, **11**, 55–75.
- 45 Frens, G. (1973) Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nat. Phys. Sci.*, **241**, 20–22.
- 46 Kimling, J., Maier, M., Okenve, B., Kotaidis, V., Ballot, H., and Plech, A. (2006) Turkevich method for gold nanoparticle synthesis revisited. *J. Phys. Chem. B*, **110**, 15700–15707.
- 47 Zhou, Q.F., Bao, J.C., and Xu, Z. (2002) Shape-controlled synthesis of nanostructured gold by a protection–reduction technique. *J. Mater. Chem.*, **12**, 384–387.
- 48 Taheri, S.M., Fischer, S., and Förster, S. (2011) Routes to nanoparticle-polymer superlattices. *Polymers*, **3**, 662–673.
- 49 Jana, N.R., Gearheart, L., and Murphy, C.J. (2001) Seed-mediated growth approach for shape-controlled synthesis of spheroidal and rod-like gold nanoparticles using a surfactant template. *Adv. Mater.*, **13**, 1389–1393.
- 50 Kim, F., Connor, S., Song, H., Kuykendall, T., and Yang, P. (2004) Platonic gold nanocrystals. *Angew. Chem.*, **116**, 3759–3763.
- 51 Zhou, M., Wang, B., Rozynek, Z., Xie, Z., Fossum, J.O., Yu, X., and Raaen, S. (2009) Minute synthesis of extremely stable gold nanoparticles. *Nanotechnology*, **20**, 505606-1–505606-10.
- 52 Young, J.K., Lewinski, N.A., Langsner, R.J., Kennedy, L.C., Satyanarayan, A., Nammalcar, V., Lin, A.Y., and Drezek, R.A. (2011) Size-controlled synthesis of monodispersed gold nanoparticles via carbon monoxide gas reduction. *Nanoscale Res. Lett.*, **6**, 428-1–428-11.

5

3D Printing via Multiphoton Polymerization

Maria Farsari

Recent progress in technologies such as MEMS and microfluidics has increased the requirement for 3D printing technologies with micro- and nanofeature resolution, using diverse materials, such as ceramics and polymers. In this chapter, we describe a microfabrication technique based on laser technologies: multiphoton lithography.

Multiphoton lithography (MPL), based on the multiphoton polymerization of photosensitive materials, is a direct laser writing technique that allows the fabrication of three-dimensional structures with submicron resolution [1–5]. The polymerization is based on two-photon absorption; when the beam of an ultrafast laser is tightly focused into the volume of a transparent, photosensitive material, the polymerization process can be initiated by nonlinear absorption within the focal volume. By moving the laser focus three dimensionally through the material, 3D structures can be fabricated. The technique has been implemented with a variety of acrylate and epoxy materials, and several components and devices have been fabricated such as photonic crystal templates [6], mechanical devices [7], and microscopic models [8]. Resolution below 100 nm has been achieved using this technique [9].

The unique capability of MPL lies in that it allows the fabrication of computer-designed, fully 3D structures with resolution beyond the diffraction limit. No other competing technology offers these advantages. Classic 3D prototyping techniques such as UV laser stereolithography, 3D inkjet printing, and laser sintering can also produce fully 3D structures; however, they cannot provide resolution better than a few microns. On the other hand, lithographic techniques with superior resolution, such as e-beam lithography, cannot produce anything more complicated than high-aspect-ratio two-dimensional structures.

In what follows, we summarize the principles of microfabrication by MPL. We discuss the fundamental principles of multiphoton absorption and describe a typical MPL experimental setup. Then, we concentrate on the materials used for MPL microfabrication, on recent progress in the functionalization of the surface, and the bulk of the 3D-fabricated structures at the same time discussing applications of the technology.

5.1 Multiphoton Polymerization

The basis of MPL is the phenomenon of multiphoton absorption (MPA). For simplicity, we discuss two-photon absorption (TPA) and two-photon polymerization (TPP) – the same rules apply to more than two photons.

There are two types of two-photon absorption: sequential and simultaneous. In sequential absorption, the absorbing species is excited to a real intermediate energy state, and then a second photon is absorbed. The presence of the intermediate energy state implies that the material absorbing at this specific wavelength; it will therefore be a surface effect and will follow the Beer–Lambert law [10]. The simultaneous absorption, on which the MPL technique is based, was originally predicted by Maria Göppert-Mayer in 1931 in her doctoral dissertation [11]. It is defined as “an absorption event caused by the collective action of two or more photons, all of which must be present simultaneously to impart enough energy to drive a transition”. This prediction was not experimentally verified until over 30 years later by Werner Kaiser, when the invention of the laser permitted the first experimental verification of the TPA when two-photon excited fluorescence was detected in a europium-doped crystal [12]. In simultaneous absorption, there is no real intermediate energy state; that is, the material is transparent at that wavelength. Instead, there is a virtual intermediate energy state, and two-photon absorption happens only if another photon arrives within the virtual state lifetime [13]. For this to occur, high intensities are required, which can only be provided by a tightly focused femtosecond laser beam. This is illustrated in Figure 5.1; as it can be seen, the electron transition in this case is caused by two photons of energy $h\nu/2$ rather than one of energy $h\nu$.

Ti:sapphire and near-infrared lasers are widely used for this purpose. They have two main advantages: first, they have very short pulses, in the order of a few tens of femtoseconds, so they do not cause thermal damage. Second, their standard wavelength is 780–820 nm, which is twice the wavelength of polymerization of a wide range of photopolymers. In addition, most photopolymers are transparent at around 800 nm, which allows in-volume focusing of the laser beam with minimal scattering.

Photopolymerization is a light-induced reaction, which converts a liquid or gel monomer into a solid polymer. These reactions require the use of an appropriate photoinitiator, which is a light-sensitive molecule that produces an active species

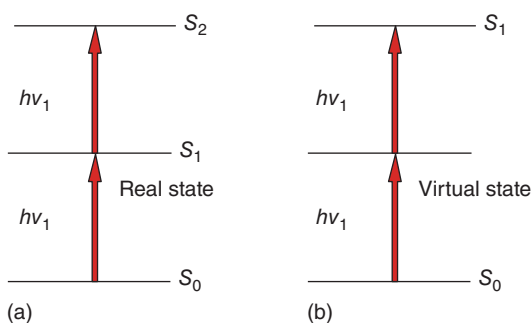


Figure 5.1 Sequential (a) and simultaneous absorption (b). In the first case, the intermediate energy level is an actual energy level, while in the second case it is virtual.

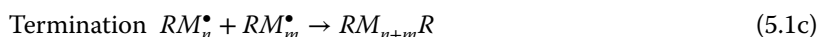
upon irradiation with UV, visible, or infrared light. The photoinitiators that have been most extensively used so far are divided into two main categories depending on the nature of generated active species (radicals or cations). An effective initiator has a high quantum yield in the generation of the active moieties, high thermal stability, and stability in darkness and is highly soluble in the polymerization medium.

Free-radical polymerizations are chain reactions in which the addition of a monomer molecule to an active chain-end regenerates the active site at the chain-end.

The free-radical photopolymerization mechanism involves at least three different kinds of reactions [14–16], (Equation 5.1):

- Step 1a: The first step is the initiation during which the free-radical initiator is decomposed with light in the presence of monomer to form an active species.
- Step 1b: In the next step, known as propagation, the initiator fragment reacts with a monomer molecule to form the first active adduct that is capable of being polymerized. Monomers continue to add in the same manner resulting in the formation of macroradicals, which are end-active polymers.
- Step 1c: The final step is the termination during which the growth center is deactivated and the final polymer molecules are formed. This step normally involves the reaction between two polymers bearing active centers and can proceed by two different mechanisms – combination or disproportionation – leading to the formation of one or two polymers chains, respectively.

The two-photon polymerization process



Besides these, other reactions, such as chain transfer and chain inhibition, often take place and complicate the mechanism of free-radical polymerization.

Photopolymerizations follow the general scheme for any polymerization; however, the use of light, rather than heat, to drive the reaction has certain advantages, such as the elimination of solvent, the high reaction rates at room temperature, and the spatial control of the polymerization. When the laser is focused tightly into the material, the photoinitiator used to initiate the polymerization will absorb two or more photons and produce radicals. As the material response is proportional to the square of the intensity, this will only happen at the focal point, which, combined with the fact that the two-photon transition rate is very small, will provide very high spatial resolution.

5.2 The Diffraction Limit

Theoretically, the highest resolution that can be achieved by a focused laser beam is given by Abbe's diffraction limit [17] (Equation (5.2))

Abbe's diffraction limit (Equation (5.2))

$$\text{Diffraction Limit} = \frac{0.5\lambda}{N.A.} \quad (5.2)$$

where λ is the laser wavelength and $N.A.$ is the numerical aperture of the focusing objective; this has fueled the race for ever-decreasing wavelengths, such as electron wavelengths and for alternative, non-light-patterning techniques such as atomic force microscopy (AFM) [18–22] and near-field scanning optical microscopy (NSOM) [23–25]; however, these techniques only allow surface and not in-volume patterning. To produce 3D structures with in-volume patterning and produce photopolymerized voxels smaller than that defined by the diffraction limit, materials with well-defined photopolymerization threshold need to be used.

As the photoinitiator is excited by the laser process, it produces radicals; these radicals are quenched by oxygen and other quenchers in the system. Quenching is a competing effect to photopolymerization and is usually considered detrimental to the process. In MPL, however, it can be used to circumvent the diffraction limit and produce structures of very high resolution. This can be done by modifying the light intensity at the focal volume, in a manner so that the light-produced radicals exceed the quenchers and initiate polymerization only at a region where exposure energy is larger than the threshold. In this case, the diffraction limit becomes just a measure of the focal spot size and it does not really determine the voxel size.

5.3 Experimental Setup

A typical experimental setup for the fabrication of three-dimensional microstructures by MPL is shown in Figure 5.2. The laser source typically is a Ti:sapphire femtosecond oscillator operating at 800 nm; there are also examples in literature where an optical parametric oscillator (OPO) is used with a Ti:sapphire laser to reduce the laser wavelength to visible wavelengths [9, 26]. The laser will typically have a pulse length of less than 200 fs and a repetition rate of 50–80 MHz. The energy required for the polymerization process will depend on the material, the photoinitiator, and the focusing, but it is usually in the order of a few nanojoules per pulse.

The photopolymerized structure is usually generated in a layer-by-layer format. Each layer is formed either using an x – y galvanometric mirror scanner or x – y piezoelectric stages. The main difference between the two cases is that in the former case, the structure remains immobile and the structure is generated by the laser beam moving, while in the latter case the x – y stages move the structure and the laser beam remains immobile. Movement on the z -axis can be achieved using a piezoelectric or a high-resolution linear stage.

To achieve the tight focusing conditions required for two-photon polymerization to occur, a microscope objective needs to be used; when the numerical aperture (N.A.) of the objective is higher than 1, immersion oil is used for index matching. Galvo scanners have to be adapted to accommodate microscope objectives, as they are usually designed to take lenses with long focal lengths.

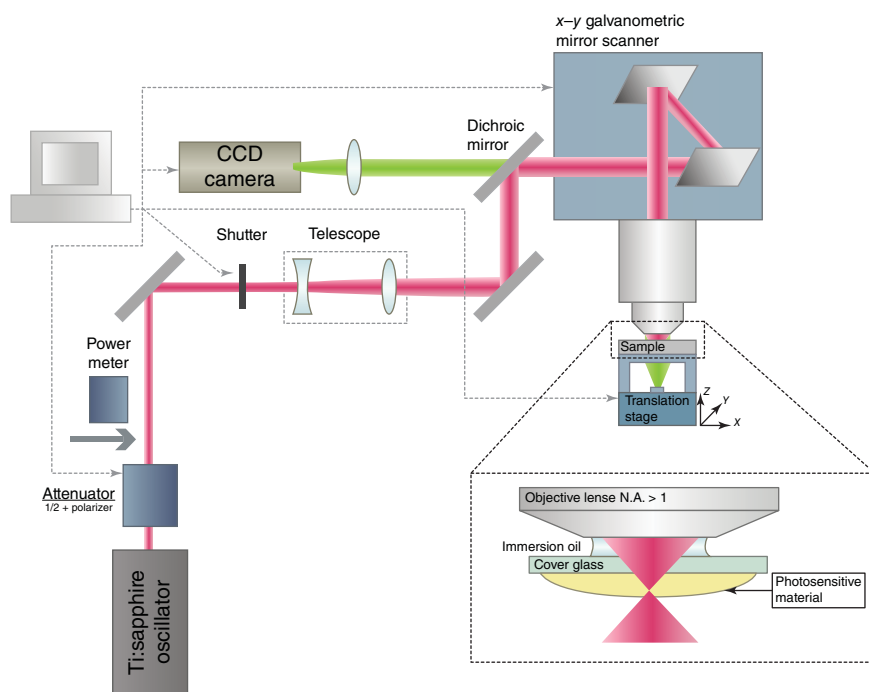


Figure 5.2 A typical setup for multiphoton polymerization, consisting of an fs laser, a galvanometric mirror scanner, moving stages, directional and focusing optics, and a monitoring camera.

Beam control can be achieved by either using a fast mechanical shutter or an acousto-optic modulator, while beam intensity control can be achieved using neutral density filters, a variable attenuator or a combination of a polarizer and a waveplate.

For online monitoring of the photopolymerization process, a CCD camera can be mounted behind a dichroic mirror, as shown in Figure 5.2. This is possible as the refractive index of most photopolymers changes during polymerization, so that the illuminated structures become visible during the building process.

When the photosensitive polymer is in a liquid form, in order to avoid liquid movement as the samples move, the samples are prepared in a sandwich format between two thin glass coverslips; a spacer needs to be used to maintain sample uniformity. When the sample is a solid or a gel, then there is no need for the sandwich format. To avoid the distortion of the focused laser beam by the built structures, they are fabricated layer-by-layer bottom-up with the last layer attached to the glass coverslip.

After the completion of the photopolymerization process and in order to remove the unphotopolymerized resin, the samples need to be developed as in any lithographic process. The developer used and the time for development will depend on the material.

The experimental procedure for fabricating a 3D structure by MPL is shown in Figure 5.3. (a) The laser beam is tightly focused into the volume of the material.

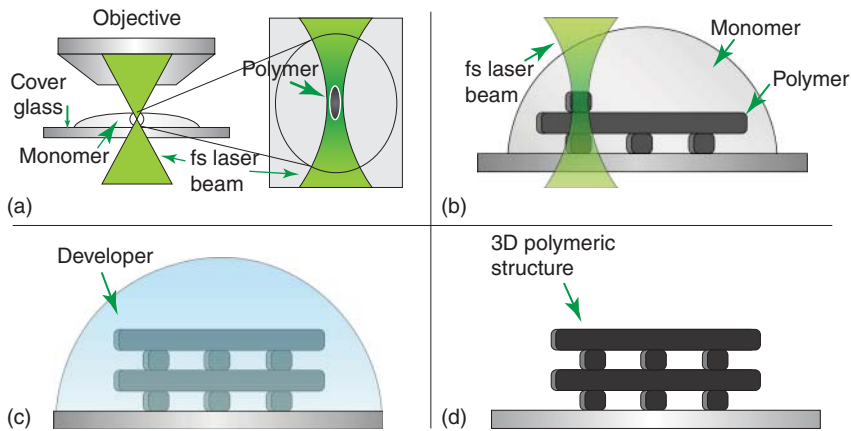


Figure 5.3 MPL experimental procedure: (a) beam focusing, (b) laser writing, (c) development, (d) completed structure.

(b) Either the focused beam or the sample moves following a computer-generated pattern. (c) After the laser writing of the structure, the sample is immersed into an appropriate developer. (d) The free-standing structure is revealed.

5.4 Materials for MPP

5.4.1 Introduction

In general, a material suitable for structuring with MPL includes at least two components: (i) a monomer, or a mixture of monomers/oligomers, which will provide the final polymer and (ii) a photoinitiator, which will absorb the laser light and provide the active species that will cause this polymerization. Several monomer/oligomer and photoinitiator combinations have been used for this purpose. These are mostly negative photoresists such as hydrogels, acrylate materials [27, 28], the epoxy-based photoresist SU-8 [2], and hybrid materials [3, 29]. Recently, redox and Diels–Alder photopolymerization reactions have been also been reported [30, 31]. In the following sections, we discuss briefly these photoinitiators and materials.

5.4.2 Photoinitiators

During polymerization, a monomer is converted into polymer and this transformation can be induced by light. In classic photolithography, a photoinitiator absorbs the light and produces an active species, which causes the photopolymerization. In two-photon polymerization, however, things are more complicated, and the following additional requirements must be fulfilled [1, 27]:

- Both the photoinitiator and the monomer/oligomer are transparent at the laser wavelength used, so that the laser beam can be focused inside the volume of the material without being absorbed at the surface.

- The monomer/oligomer needs to be transparent at the two-photon absorption wavelength ($\lambda/2$); if not, then the photopolymer is likely to be burnt or ablated.
- The photoinitiator needs not only to absorb at the two-photon wavelength but also to have a high two-photon cross section, a high radical quantum yield, and highly active radical species generated; typically, if any two of these three are large enough, the initiator will normally be efficient for two-photon polymerization.

In classic lithography, there are two types of photoinitiators: radical photoinitiators and cationic photoinitiators. All the materials developed to date for MPL employ radical photoinitiators. These photoinitiators, upon light irradiation, generate free radicals, which initiate a polymerization process of acrylates or vinyl ethers. Cationic initiators are photoacid generators that produce cations upon light irradiation and are used for the polymerization of epoxides or vinyl ethers [14–16]; to the best of our knowledge, there are no materials to date, specifically developed for MPL employing cationic polymerization; however, it is employed in the most commonly used photolithography resist SU-8.

An effective MPL photoinitiator has a high quantum yield in the generation of the active moieties, high thermal stability and stability in darkness, and is highly soluble in the polymerization medium [32]. The most commonly used free-radical photoinitiator is benzophenone and its derivatives [33, 34].

Nowadays, there are many concentrated efforts to synthesize fast and efficient photoinitiators specifically for multiphoton applications [35]. In addition, there is a lot of work toward biocompatible photoinitiators, specifically for bioapplications. To this end, classic dyes such as Bengal rose, eosin, Nile red, biomolecules such as flavin mononucleotide, and also novel, synthetic photoinitiators have been used [28, 32, 36–42].

5.4.3 Organic Photopolymers

The first materials used for MPL were acrylate photopolymers [43, 44] (Figure 5.4). These materials have several properties that make them attractive for MPL applications: a wide variety of the full composites or their monomers are commercially available; they are transparent at visible and near-infrared wavelengths and can therefore be processed by IR and green ultrafast lasers; they can be developed in common, nonaggressive solvents such as isopropanol; they can be polymerized fast and with low shrinkage; and after polymerization, they are mechanically and chemically stable.

Due to their versatile chemistry, acrylate photopolymers have been used in their pure form and also doped with other materials to add functionality. They have been doped with (i) TiO_2 nanoparticles to increase their refractive index for photonic crystal applications [45]; (ii) CdS nanoparticles for the fabrication of light-emitting 3D structures [46, 47]; (iii) metal-binding materials to cover them with metals using electroless plating [48, 49]; (iv) chitosan to make them suitable for bioapplications [50]; and (v) MEH-PPV to make them electroluminescent [51].

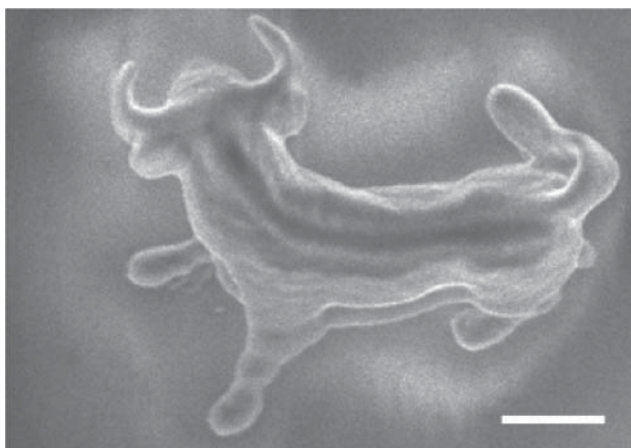


Figure 5.4 One of the first 3D structures fabricated by MPL. (Kawata *et al.* (2001) [44]. Reproduced with permission of Nature Publishing.)

5.4.4 SU-8

SU-8 is a negative, epoxy-based photoresist commonly used for the fabrication of high-aspect-ratio structures, using standard contact lithography. Its absorption maximum is at 365 nm. When exposed to the right light, SU-8's long molecular chains cross link, causing the material to become insoluble in most common solvents. For this to happen, the SU-8 films require postexposure heat treatment.

The possibility to structure SU-8 by MPL polymerization was first demonstrated by Witzgall *et al.*, who employed single shots from Ti:sapphire femtosecond amplifier to fabricate small dots [52]. More complex 2D and 3D structures were built by Belfield *et al.* and Kuebler *et al.*, respectively, who worked on the development of novel, efficient photoinitiators for cationic polymerization [53, 54]. Since then, SU-8 has been used by numerous research teams involved in MPL fabrication [55–59].

SU-8 is thermally stable, transparent in the visible, and highly resistant to solvents, acids, and bases. These properties make it suitable for permanent use application; by itself, SU-8 has been employed for the fabrication of photonic [8, 60] (Figure 5.5), microfluidic [61–63], and biomedical structures [64], while it has also been covered with metal for metamaterial fabrication.

5.4.5 Hybrid Materials

Over the last few years, there has been a lot of research on the development of photosensitive hybrid composites for MPL. Especially, silicate-only-based photopolymers have proved to be a very popular choice, as they can be commercially available and they combine properties of silicate glasses such as hardness, chemical and thermal stability, and optical transparency with the laser processing at low temperatures of organic polymers, which are the properties impossible to achieve with just inorganic or polymeric materials [26, 65–81]. The most widely used

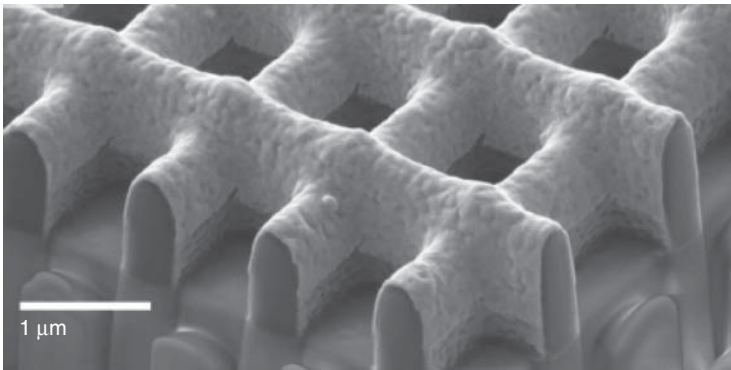


Figure 5.5 A photonic structure fabricated using SU-8. (Rill *et al.* (2009) [60]. Reproduced with permission of The Optical Society.)

and studied silicate material is the photopolymer ORMOCER®, commercially available from Microresist Technologies, Germany, and it has been used for a variety of mostly photonic applications, such as the microneedles shown in Figure 5.6 [82].

ORMOCER® and other silicate-only-based hybrid materials have provided the possibility to fabricate high-resolution 3D structures; they do not allow, however, optimization and “fine-tuning” of the materials properties for specific applications. The versatile chemistry of hybrid composites allows the copolymerization of more than one metal alkoxides; this has been shown to enhance the material’s mechanical stability and allow the modification of its optical properties. There are a few examples of composite photosensitive hybrid materials used in MPL applications [3, 34, 83, 84]; Ovsianikov *et al.* showed that under specific fluence conditions, specific material combinations can be structured into complex 3D structures without shrinkage [85, 86]. In addition to metal alkoxides, hybrid materials chemistry provides the possibility of the inclusion of functional groups, such as nonlinear optical molecules [87, 88], quantum dots [89], and metal-binding materials [90]. Zirconium silicates doped with a monomer containing amine moieties were used for the fabrication for the first time using MPL of 3D structures selectively metalized with silver (Figure 5.7) [91, 92].

5.4.6 Applications

5.4.6.1 Metamaterials

Metamaterials are artificial materials with properties that do not exist in nature; these properties are due to structure and not material composition. Their name derives from the Greek word “meta”, which means beyond, because these materials have properties that extend beyond that of materials found naturally. In metamaterials, an assembly of structures can replace the role that atoms and molecules have in conventional materials, resulting in a composite structure with electromagnetic properties beyond anything that can be found naturally or chemically synthesized.

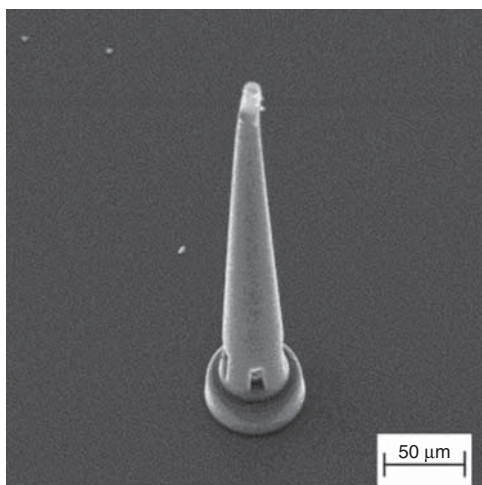
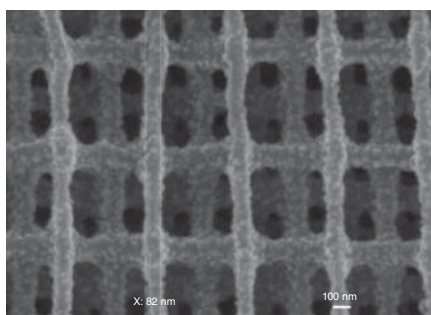
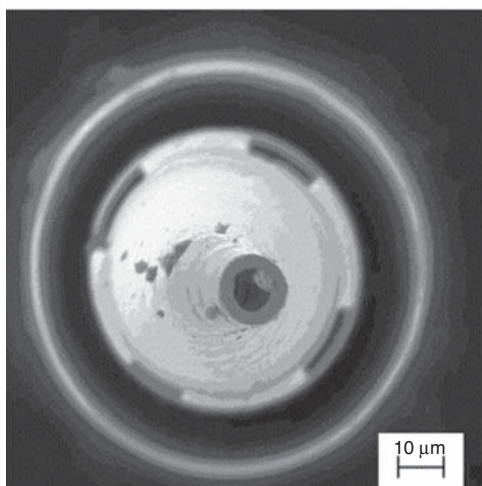
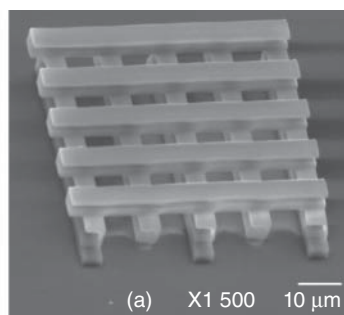


Figure 5.6 A microneedle fabricated using ORMOCER®. (Doraiswamy *et al.* (2006) [82]. Reproduced with permission of Elsevier.)



(a)



(b)

Figure 5.7 A three-dimensional photonic crystal with sub-100 nm features (a). (Vasilantonakis *et al.* (2012) [91]. Reproduced with permission of Wiley.) An IR polarizer (b). (Kenanakis *et al.* (2015) [92]. Reproduced with permission of American Chemical Society.)

Photonic metamaterials consist of nanostructured metallodielectric subwavelength building components and allow the realization of many new and unusual optical properties, such as negative refractive index, magnetism at optical frequencies, perfect absorption, and enhanced optical nonlinearities. Several applications of metamaterials have been proposed, including ultrahigh-resolution imaging systems, compact polarization optics, and cloaking devices ([93] and references herein). The realization of these applications requires the fabrication of large-scale metallodielectric structures, a very challenging task. There has been some limited research into the direct fabrication of metallic 3D structures using multiphoton reduction of metal ions. The quality of the structures, however, has been compromised by the reduced transparency of the metal ion solutions at the laser wavelengths used (500–800 nm) [94, 95]. Metallic woodpile structures have also been realized experimentally at micron wavelengths using traditional lithographic techniques [96–98]. However, lithographic techniques can accommodate only a very limited number of layers, and aligning each layer with the previous one is difficult.

MPL is the only inherent 3D fabrication technique, with the potential to fabricate 3D structures, but the majority of the materials structurable by MPL are dielectrics. A popular approach is to use MPL to make dielectric structures, and subsequently metalize them. The most successful approaches and their advantages and disadvantages are listed as follows:

- 1) *MPL of positive photoresists and filling with gold using electroplating* [99, 100]. Here, voids are created in a positive tone photoresist using MPL; these are subsequently filled with gold using classic electroplating. The main advantage of this technique is that there is no need to remove the photoresist as the refractive index contrast between the gold and the dielectric material is very high. The main disadvantage is that the number of designs that can be structured is limited, as the right apertures of the material removal and gold filling have to be allowed; therefore, this is fundamentally a 2.5D structuring technique.
- 2) *MPL of dielectric structures and nonselective metallization with electroless plating*. Here, a standard photolithographic material is used, such as SU-8, for the fabrication of the structures, and subsequently their surface is covered with silver using classic electroless plating [101–104]. Additional processing, to enable the metal adhesion on the surface, is required, and the quality, structural integrity, and resolution of the structures depend on the building material and the surface-processing step. The advantage of this technique is that any photopolymer can be used; the disadvantages are that, as the density of the metal-binding sites on the structure cannot be controlled, the metallization quality can vary. In addition, along with the surface of the structures, the substrate is also activated; the metallization is therefore not selective, often requiring an extra step to remove the structures from the metalized substrate [102].
- 3) *MPL of dielectric structures and selective metallization with electroless plating*. Here, a composite doped with the metal-binding sites is employed for the structure fabrication [49, 90, 91]. The main advantages in this case are that the metallization is selective, and the density and distribution of

the metal-binding sites can be controlled. The main disadvantages are that specific metal-binding materials need to be used, and in most cases these were not able to provide the required resolution and structural integrity required for optical metamaterials. Only very recently it was shown that it is possible to use this method for the fabrication of optical nanophotonic devices [91].

- 4) *MPL of dielectric structures and metallization with chemical vapor deposition (CVD)*. Here, MPL is used to fabricate 3D structures by any material, typically SU-8 [105]. The surface of the structures is subsequently activated using plasma etch. Finally, they are covered with silver using CVD. The main advantage of this technique is that any photopolymer can be used, and the resolution and final quality of the structures will depend on the photopolymer used. The main disadvantages are as follows: first, CVD can only penetrate a small number of structure layers, allowing only a small number of unit cells, and second, there is no selectivity, as with the plasma etch, the substrate is activated as well as the structure.

It should also be noted that there has been some recent work on structuring by MPL transparent conducting materials, such as ionogels [106, 107]. However, neither the conductivity nor the resolution of these materials is sufficient for applications in metamaterials.

5.4.6.2 Biomedical Applications

The biomedical applications of MPL can be broadly divided into two categories: biomedical microdevices and scaffolds for cell culture.

The first category, biomedical microdevices, includes devices such as microneedles for drug delivery and micromechanic, microfluidic, or optofluidic functional devices [108, 109]. Despite the enormous potential of 3D nanostructuring in this field, there are only few examples to date, mostly because there has not been much research into the integration of MPL-made structure into existing micromechanical systems. Only recently, Amato *et al.* employed MPL to build a cell sorter inside a commercial microfluidic chip [110, 111]. Most other structures reported are free standing and have not been integrated into a functional device [112–119].

The second category, MPL scaffolds for cell culture studies and tissue engineering, has seen an enormous growth over the last few years (Figures 5.8 and 5.9) [120, 121]. Tissue engineering is the discipline applying the principles of engineering and life sciences toward the development of biological substitutes that restore, maintain, or improve tissue function or a whole organ [122]. An important part of the development of artificial tissue is the choice of scaffold, as it can influence the attachment, migration, and proliferation of cells. 3D cell cultures offer a realistic environment where the functional properties of cells can be observed and manipulated [123–125]. Although producing scaffolds using laser-based, user-controlled manufacturing techniques such as MPL or classic stereolithography is time consuming and therefore costly, recent studies have shown that they can provide tissue engineering solutions for aligned and complex tissue growth. An important advantage is that a controlled topological environment for cell growth can be achieved (Figure 5.9). In addition, ordered

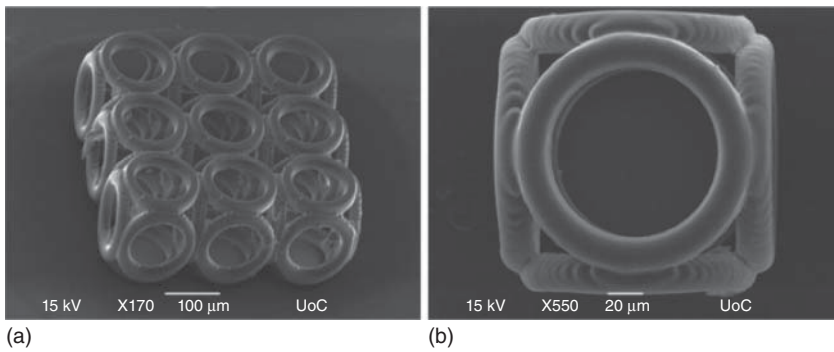


Figure 5.8 SEM images of a 3D artificial scaffold. (Chatzinikolaidou *et al.* (2015) [120]. Reproduced with permission of Elsevier.)

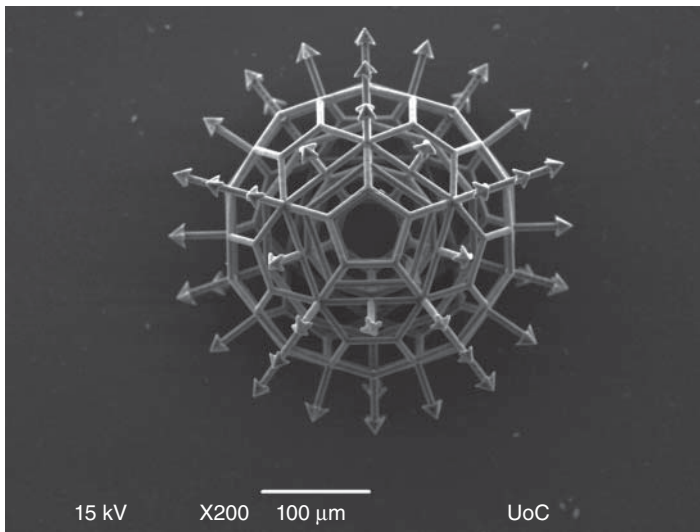


Figure 5.9 A free-standing microsphere scaffold. (Danilevicius *et al.* (2015) [121]. Reproduced with permission of American Institute of Physics.)

3D scaffolds are ideally suited for exploring the relationship between 3D topology and cell proliferation. The possibility to manipulate particles in an aqueous solution in order to produce composite material scaffolds with different biological properties selectively localized in space is another advantage of MPL [126].

Recent reviews by Raimondi *et al.* [127], Ovsianikov *et al.* [128], and Selimis *et al.* [4] describe the use of lasers in tissue engineering applications in great detail. In this field, most groups have used permanent scaffolds for hard tissue engineering or investigating cell (including stem cell) growth [50, 64, 120, 121, 129–138]. More recently, there has been a lot of active research into the synthesis of new biocompatible and biodegradable materials [33, 139–141].

5.5 Conclusions

Multiphoton lithography allows the fabrication of fully three-dimensional structures with subdiffraction limit resolution. While up to recently most research efforts have involved the use of materials for conventional one-photon lithography, the potential of new, tailor-made hybrid materials for MPL fabrication has started to emerge allowing them in applications such as photonics, metamaterials, and biomedical implants.

References

- 1 Sun, H.-B. and Kawata, S. (2004) Two-Photon Photopolymerization and 3D Lithographic Microfabrication, in *NMR 3D Analysis Photopolymerization* (ed. N. Fatkullin), Springer, Berlin/Heidelberg, pp. 169–273.
- 2 Juodkazis, S., Mizeikis, V., and Misawa, H. (2009) Three-dimensional micro-fabrication of materials by femtosecond lasers for photonics applications. *J. Appl. Phys.*, **106**, 051101.
- 3 Farsari, M. and Chichkov, B.N. (2009) Two-photon fabrication. *Nat. Photonics*, **3**, 450–452.
- 4 Selimis, A., Mironov, V., and Farsari, M. (2015) Direct laser writing: Principles and materials for scaffold 3D printing. *Microelectron. Eng.*, **132**, 83–89.
- 5 Malinauskas, M., Farsari, M., Piskarskas, A., and Juodkazis, S. (2013) Ultra-fast laser nanostructuring of photopolymers: A decade of advances. *Phys. Rep.*, **533**, 1–31.
- 6 Deubel, M., Wegener, M., Linden, S., von Freymann, G., and John, S. (2006) 3D-2D-3D photonic crystal heterostructures fabricated by direct laser writing. *Opt. Lett.*, **31**, 805–807.
- 7 Galajda, P. and Ormos, P. (2002) Rotation of microscopic propellers in laser tweezers. *J. Opt. B: Quantum Semiclassical Opt.*, **4**, S78–S81.
- 8 Deubel, M., Von Freymann, G., Wegener, M., Pereira, S., Busch, K., and Soukoulis, C.M. (2004) Direct laser writing of three-dimensional photonic-crystal templates for telecommunications. *Nat. Mater.*, **3**, 444–447.
- 9 Haske, W., Chen, V.W., Hales, J.M., Dong, W.T., Barlow, S., Marder, S.R. *et al.* (2007) 65 nm feature sizes using visible wavelength 3-D multiphoton lithography. *Opt. Express*, **15**, 3426–3436.
- 10 Jacobs, P.F. (1992) *Rapid Prototyping and Manufacturing: Fundamentals of Stereolithography*, Society of Manufacturing Engineers, Dearborn, Mich..
- 11 Göppert-Mayer, M. (1931) Über Elementarakte mit zwei Quantensprüngen. *Ann. Phys.*, **401**, 273–294.
- 12 Kaiser, W. and Garrett, C.G.B. (1961) Two-photon excitation in $\text{CaF}_2:\text{Eu}^{2+}$. *Phys. Rev. Lett.*, **7**, 229–232.
- 13 Varadan, V.K., Jiang, X., and Varadan, V.V. (2001) *Microstereolithography and Other Fabrication Techniques for 3D MEMS*, John Wiley & Sons, Chichester.

- 14 Stevens, M.P. (1999) *Polymer Chemistry: An Introduction*, 3rd edn, Oxford University Press, New York.
- 15 Allcock, H.R., Lampe, F.W., and Mark, J.E. (2003) *Contemporary Polymer Chemistry*, 3rd edn, Upper-Saddle River, NJ, Pearson-Prentice Hall.
- 16 Hiemenz, P.C. and Lodge, T.P. (2007) *Polymer Chemistry*, 2nd edn, CRC Press, New York.
- 17 Born, M. and Wolf, E. (1999) *Principles of Optics*, 7th edn, Cambridge University Press.
- 18 Sauer, B.B., McLean, R.S., and Thomas, R.R. (1998) Tapping mode AFM studies of nano-phases on fluorine-containing polyester coatings and octadecyltrichlorosilane monolayers. *Langmuir*, **14**, 3045–3051.
- 19 Agarwal, G., Naik, R.R., and Stone, M.O. (2003) Immobilization of histidine-tagged proteins on nickel by electrochemical dip pen nanolithography. *J. Am. Chem. Soc.*, **125**, 7408–7412.
- 20 Amro, N.A., Xu, S., and Liu, G.Y. (2000) Patterning surfaces using tip-directed displacement and self-assembly. *Langmuir*, **16**, 3006–3009.
- 21 Garino, J.C., Yang, Y.Y., Amro, N.A., Cruchon-Dupeyrat, S., Chen, S.W., and Liu, G.Y. (2003) Precise positioning of nanoparticles on surfaces using scanning probe lithography. *Nano Lett.*, **3**, 389–395.
- 22 Liang, J. and Scoles, G. (2007) Nanografting of alkanethiols by tapping mode atomic force microscopy. *Langmuir*, **23**, 6142–6147.
- 23 Betzig, E. and Trautman, J.K. (1992) Near-field Optics-microscopy, spectroscopy, and surface modification beyond the diffraction limit. *Science*, **257**, 189–195.
- 24 Heinzelmann, H. and Pohl, D.W. (1994) Scanning near-field optical microscopy. *Appl. Phys. A: Mater. Sci. Process.*, **59**, 89–101.
- 25 Samori, P. (2004) Scanning probe microscopies beyond imaging. *J. Mater. Chem.*, **14**, 1353–1366.
- 26 Straub, M., Nguyen, L.H., Fazlic, A., and Gu, M. (2004) Complex-shaped three-dimensional microstructures and photonic crystals generated in a polysiloxane polymer by two-photon microstereolithography. *Opt. Mater.*, **27**, 359–364.
- 27 LaFratta, C.N., Fourkas, J.T., Baldacchini, T., and Farrer, R.A. (2007) Multi-photon fabrication. *Angew. Chem., Int. Ed.*, **46**, 6238–6258.
- 28 Farsari, M., Filippidis, G., Sambani, K., Drakakis, T.S., and Fotakis, C. (2006) Two-photon polymerization of an Eosin Y-sensitized acrylate composite. *J. Photochem. Photobiol., A*, **181**, 132–135.
- 29 Farsari, M., Vamvakaki, M., and Chichkov, B.N. (2010) Multiphoton polymerization of hybrid materials. *J. Opt.*, **12**, 12.
- 30 Kabouraki, E., Giakoumaki, A.N., Danilevicius, P., Gray, D., Vamvakaki, M., and Farsari, M. (2013) Redox multiphoton polymerization for 3D nanofabrication. *Nano Lett.*, **13**, 3831–3835.
- 31 Quick, A.S., Rothfuss, H., Welle, A., Richter, B., Fischer, J., Wegener, M. *et al.* (2014) Fabrication and spatially resolved functionalization of 3D microstructures via multiphoton-induced Diels–Alder chemistry. *Adv. Funct. Mater.* **24**, 3571–3580.

- 32 Li, Z., Pucher, N., Cicha, K., Torgersen, J., Ligon, S.C., Ajami, A. *et al.* (2013) A straightforward synthesis and structure-activity relationship of highly efficient initiators for two-photon polymerization. *Macromolecules*, **46**, 352–361.
- 33 Claeysens, F., Hasan, E.A., Gaidukeviciute, A., Achilleos, D.S., Ranella, A., Reinhardt, C. *et al.* (2009) Three-dimensional biodegradable structures fabricated by Two-photon polymerization. *Langmuir*, **25**, 3219–3223.
- 34 Bhuian, B., Winfield, R.J., O'Brien, S., and Crean, G.M. (2006) Investigation of the two-photon polymerisation of a Zr-based inorganic–organic hybrid material system. *Appl. Surf. Sci.*, **252**, 4845–4849.
- 35 Lu, W.-E., Dong, X.-Z., Chen, W.-Q., Zhao, Z.-S., and Duan, X.-M. (2011) Novel photoinitiator with a radical quenching moiety for confining radical diffusion in two-photon induced photopolymerization. *J. Mater. Chem.*, **21**, 5650–5659.
- 36 Xing, J., Liu, J., Zhang, T., Zhang, L., Zheng, M.-L., and Duan, X.-M. (2014) A water soluble initiator prepared through host-guest chemical interaction for microfabrication of 3D hydrogels via two-photon polymerization. *J. Mater. Chem. B*, **2**, 4318–4323.
- 37 Pitts, J.D., Howell, A.R., Taboada, R., Banerjee, I., Wang, J., Goodman, S.L. *et al.* (2002) New photoactivators for multiphoton excited three-dimensional submicron cross-linking of proteins: Bovine serum albumin and type 1 collagen. *Photochem. Photobiol.*, **76**, 135–144.
- 38 Nazir, R., Danilevicius, P., Gray, D., Farsari, M., and Gryko, D.T. (2013) Push-pull acylo-phosphine oxides for two-photon-induced polymerization. *Macromolecules*, **46**, 7239–7244.
- 39 Nazir, R., Danilevicius, P., Ciuciu, A., Chatzinikolaidou, M., Gray, D., Flamigni, L. *et al.* (2014) π -Expanded keto-coumarins as efficient, bio-compatible initiators for two-photon induced polymerization. *Chem. Mater.*, **26** (10), 3175–3184.
- 40 Li, Z.Q., Torgersen, J., Ajami, A., Muhleder, S., Qin, X.H., Husinsky, W. *et al.* (2013) Initiation efficiency and cytotoxicity of novel water-soluble two-photon photoinitiators for direct 3D microfabrication of hydrogels. *RSC Adv.*, **3**, 15939–15946.
- 41 Nazir, R., Bourquard, F., Balčiūnas, E., Smoleń, S., Gray, D., Tkachenko, N.V. *et al.* (2015) π -Expanded α,β -unsaturated ketones: Synthesis, optical properties, and two-photon-induced polymerization. *ChemPhysChem*, **16**, 682–690.
- 42 Nazir, R., Balčiūnas, E., Buczyńska, D., Bourquard, F., Kowalska, D., Gray, D. *et al.* (2015) Donor–acceptor type thioxanthenes: Synthesis, optical properties, and two-photon induced polymerization. *Macromolecules*, **48**, 2466–2472.
- 43 Maruo, S., Nakamura, O., and Kawata, S. (1997) Three-dimensional micro-fabrication with two-photon-absorbed photopolymerization. *Opt. Lett.*, **22**, 132–134.
- 44 Kawata, S., Sun, H.B., Tanaka, T., and Takada, K. (2001) Finer features for functional microdevices - Micromachines can be created with higher resolution using two-photon absorption. *Nature*, **412**, 697–698.

- 45 Duan, X.M., Sun, H.B., Kaneko, K., and Kawata, S. (2004) Two-photon polymerization of metal ions doped acrylate monomers and oligomers for three-dimensional structure fabrication. *Thin Solid Films*, **453–54**, 518–521.
- 46 Sun, Z.B., Dong, X.Z., Chen, W.Q., Nakanishi, S., Duan, X.M., and Kawata, S. (2008) Multicolor polymer nanocomposites: In situ synthesis and fabrication of 3D microstructures. *Adv. Mater.*, **20**, 914–919.
- 47 Sun, Z.B., Dong, X.Z., Chen, W.Q., Shoji, S., Duan, X.M., and Kawata, S. (2008) Two- and three-dimensional micro/nanostructure patterning of CdS-polymer nanocomposites with a laser interference technique and in situ synthesis. *Nanotechnology*, **19**, 035611.
- 48 Formanek, F., Takeyasu, N., Tanaka, T., Chiyoda, K., Ishikawa, A., and Kawata, S. (2006) Selective electroless plating to fabricate complex three-dimensional metallic micro/nanostructures. *Appl. Phys. Lett.*, **88**, 3.
- 49 Takeyasu, N., Tanaka, T., and Kawata, S. (2008) Fabrication of 3D metal/polymer microstructures by site-selective metal coating. *Appl. Phys. A: Mater. Sci. Process.*, **90**, 205–209.
- 50 Correa, D.S., Tayalia, P., Cosendey, G., dos Santos, D.S., Aroca, R.F., Mazur, E. *et al.* (2009) Two-photon polymerization for fabricating structures containing the biopolymer chitosan. *J. Nanosci. Nanotechnol.*, **9**, 5845–5849.
- 51 Mendonca, C.R., Correa, D.S., Marlow, F., Voss, T., Tayalia, P., and Mazur, E. (2009) Three-dimensional fabrication of optically active microstructures containing an electroluminescent polymer. *Appl. Phys. Lett.*, **95**, 113309.
- 52 Witzgall, G., Vrijen, R., Yablonovitch, E., Doan, V., and Schwartz, B.J. (1998) Single-shot two-photon exposure of commercial photoresist for the production of three-dimensional structures. *Opt. Lett.*, **23**, 1745–1747.
- 53 Belfield, K.D., Schafer, K.J., Liu, Y.U., Liu, J., Ren, X.B., and Van Stryland, E.W. (2000) Multiphoton-absorbing organic materials for microfabrication, emerging optical applications and non-destructive three-dimensional imaging. *J. Phys. Org. Chem.*, **13**, 837–849.
- 54 Kuebler, S.M., Braun, K.L., Zhou, W.H., Cammack, J.K., Yu, T.Y., Ober, C.K. *et al.* (2003) Design and application of high-sensitivity two-photon initiators for three-dimensional microfabrication. *J. Photochem. Photobiol., A*, **158**, 163–170.
- 55 Teh, W.H., Durig, U., Salis, G., Harbers, R., Drechsler, U., Mahrt, R.F. *et al.* (2004) SU-8 for real three-dimensional subdiffraction-limit two-photon microfabrication. *Appl. Phys. Lett.*, **84**, 4095–4097.
- 56 Juodkasis, S., Mizeikis, V., Seet, K.K., Miwa, M., and Misawa, H. (2005) Two-photon lithography of nanorods in SU-8 photoresist. *Nanotechnology*, **16**, 846–849.
- 57 Mizeikis, V., Seet, K.K., Juodkasis, S., and Misawa, H. (2004) Three-dimensional woodpile photonic crystal templates for the infrared spectral range. *Opt. Lett.*, **29**, 2061–2063.
- 58 Seet, K.K., Mizeikis, V., Matsuo, S., Juodkasis, S., and Misawa, H. (2005) Three-dimensional spiral-architecture photonic crystals obtained by direct laser writing. *Adv. Mater.*, **17**, 541–545.

- 59 Seet, K.K., Mizeikis, V., Juodkazis, S., and Misawa, H. (2006) Three-dimensional circular spiral photonic crystal structures recorded by femtosecond pulses. *J. Non-Cryst. Solids*, **352**, 2390–2394.
- 60 Rill, M.S., Kriegl, C.E., Thiel, M., von Freymann, G., Linden, S., and Wegener, M. (2009) Negative-index bianisotropic photonic metamaterial fabricated by direct laser writing and silver shadow evaporation. *Opt. Lett.*, **34**, 19–21.
- 61 Wu, D., Chen, Q.D., Niu, L.G., Wang, J.N., Wang, J., Wang, R. *et al.* (2009) Femtosecond laser rapid prototyping of nanoshells and suspending components towards microfluidic devices. *Lab Chip*, **9**, 2391–2394.
- 62 Kumi, G., Yanez, C.O., Belfield, K.D., and Fourkas, J.T. (2010) High-speed multiphoton absorption polymerization: Fabrication of microfluidic channels with arbitrary cross-sections and high aspect ratios. *Lab Chip*, **10**, 1057–1060.
- 63 Stoneman, M., Fox, M., Zeng, C.Y., and Raicu, V. (2009) Real-time monitoring of two-photon photopolymerization for use in fabrication of microfluidic devices. *Lab Chip*, **9**, 819–827.
- 64 Ovsianikov, A., Schlie, S., Ngezhahayo, A., Haverich, A., and Chichkov, B.N. (2007) Two-photon polymerization technique for microfabrication of CAD-designed 3D scaffolds from commercially available photosensitive materials. *J. Tissue Eng. Regen. Med.*, **1**, 443–449.
- 65 Houbertz, R., Domann, G., Cronauer, C., Schmitt, A., Martin, H., Park, J.U. *et al.* (2003) Inorganic–organic hybrid materials for application in optical devices. *Thin Solid Films*, **442**, 194–200.
- 66 Houbertz, R., Frohlich, L., Popall, M., Streppel, U., Dannberg, P., Brauer, A. *et al.* (2003) Inorganic–organic hybrid polymers for information technology: From planar technology to 3D nanostructures. *Adv. Eng. Mater.*, **5**, 551–555.
- 67 Farsari, M., Filippidis, G., and Fotakis, C. (2005) Fabrication of three-dimensional structures by three-photon polymerization. *Opt. Lett.*, **30**, 3180–3182.
- 68 Jun, Y., Nagpal, P., and Norris, D.J. (2008) Thermally stable organic–inorganic hybrid photoresists for fabrication of photonic band gap structures with direct laser writing. *Adv. Mater.*, **20**, 606–610.
- 69 Serbin, J., Egbert, A., Ostendorf, A., Chichkov, B.N., Houbertz, R., Domann, G. *et al.* (2003) Femtosecond laser-induced two-photon polymerization of inorganic–organic hybrid materials for applications in photonics. *Opt. Lett.*, **28**, 301–303.
- 70 Serbin, J. and Gu, M. (2006) Superprism phenomena in waveguide-coupled woodpile structures fabricated by two-photon polymerization. *Opt. Express*, **14**, 3563–3568.
- 71 Serbin, J. and Gu, M. (2006) Experimental evidence for superprism effects in three-dimensional polymer photonic crystals. *Adv. Mater.*, **18**, 221–224.
- 72 Li, J.F., Jia, B.H., Zhou, G.Y., Bullen, C., Serbin, J., and Gu, M. (2007) Spectral redistribution in spontaneous emission from quantum-dot-infiltrated 3D woodpile photonic crystals for telecommunications. *Adv. Mater.*, **19**, 3276–3280.

- 73 Li, J.F., Jia, B.H., and Gu, M. (2008) Engineering stop gaps of inorganic–organic polymeric 3D woodpile photonic crystals with post-thermal treatment. *Opt. Express*, **16**, 20073–20080.
- 74 Woggon, T., Kleiner, T., Punke, M., and Lemmer, U. (2009) Nanos-structuring of organic–inorganic hybrid materials for distributed feed-back laser resonators by two-photon polymerization. *Opt. Express*, **17**, 2500–2507.
- 75 Dinca, V., Kasotakis, E., Catherine, J., Mourka, A., Ranella, A., Ovsianikov, A. *et al.* (2008) Directed three-dimensional patterning of self-assembled peptide fibrils. *Nano Lett.*, **8**, 538–543.
- 76 Grossmann, T., Schleede, S., Hauser, M., Beck, T., Thiel, M., von Freymann, G. *et al.* (2011) Direct laser writing for active and passive high-Q polymer microdisks on silicon. *Opt. Express*, **19**, 11451–11456.
- 77 Brasselet, E., Malinauskas, M., Zukauskas, A., and Juodkazis, S. (2011) Photopolymerized microscopic vortex beam generators: Precise delivery of optical orbital angular momentum. *Appl. Phys. Lett.*, **97**, 211108.
- 78 Liu, Z.P., Li, Y., Xiao, Y.F., Li, B.B., Jiang, X.F., Qin, Y. *et al.* (2011) Direct laser writing of whispering gallery microcavities by two-photon polymerization. *Appl. Phys. Lett.*, **97**, 211105.
- 79 Sun, Q., Juodkazis, S., Murazawa, N., Mizeikis, V., and Misawa, H. (2010) Freestanding and movable photonic microstructures fabricated by photopolymerization with femtosecond laser pulses. *J. Micromech. Microeng.*, **20**, 035004.
- 80 Trull, J., Maigyte, L., Mizeikis, V., Malinauskas, M., Juodkazis, S., Cojocar, C. *et al.* (2011) Formation of collimated beams behind the woodpile photonic crystal. *Phys. Rev. A*, **84**, 033812.
- 81 Sakellari, I., Gaidukeviciute, A., Giakoumaki, A., Gray, D., Fotakis, C., Farsari, M. *et al.* (2010) Two-Photon Polymerization of Titanium-Containing Sol–gel Composites for Three-Dimensional Structure Fabrication. *Appl. Phys. A*, **100**, 359–364.
- 82 Doraiswamy, A., Jin, C., Narayan, R.J., Mageswaran, P., Mente, P., Modi, R. *et al.* (2006) Two photon induced polymerization of organic–inorganic hybrid biomaterials for microstructured medical devices. *Acta Biomater.*, **2**, 267–275.
- 83 Winfield, R.J., Bhuian, B., O'Brien, S., and Crean, G.M. (2007) Refractive femtosecond laser beam shaping for two-photon polymerization. *Appl. Phys. Lett.*, **90**, 111115.
- 84 Winfield, R.J., Bhuian, B., O'Brien, S., and Crean, G.M. (2007) Fabrication of grating structures by simultaneous multi-spot fs laser writing. *Appl. Surf. Sci.*, **253**, 8086–8090.
- 85 Ovsianikov, A., Viertl, J., Chichkov, B., Oubaha, M., MacCraith, B., Sakellari, L. *et al.* (2008) Ultra-low shrinkage hybrid photosensitive material for Two-photon polymerization microfabrication. *ACS Nano*, **2**, 2257–2262.
- 86 Ovsianikov, A., Xiao, S.Z., Farsari, M., Vamvakaki, M., Fotakis, C., and Chichkov, B.N. (2009) Shrinkage of microstructures produced by two-photon polymerization of Zr-based hybrid photosensitive materials. *Opt. Express*, **17**, 2143–2148.

- 87 Farsari, M., Ovsianikov, A., Vamvakaki, M., Sakellari, I., Gray, D., Chichkov, B.N. *et al.* (2008) Fabrication of three-dimensional photonic crystal structures containing an active nonlinear optical chromophore. *Appl. Phys. A: Mater. Sci. Process.*, **93**, 11–15.
- 88 Zukauskas, A., Malinauskas, M., Kontenis, L., Purlys, V., Paipulas, D., Vengris, M. *et al.* (2010) Organic dye doped microstructures for optically active functional devices fabricated via two-photon polymerization technique. *Lith. J. Phys.*, **50**, 55–61.
- 89 Jia, B., Buso, D., Embden, J., Li, J., and Gu, M. (2010) Highly non-linear quantum dot doped nanocomposites for functional three-dimensional structures generated by two-photon polymerization. *Adv. Mater.*, **22**, 2463–2467.
- 90 Terzaki, K., Vasilantonakis, N., Gaidukeviciute, A., Reinhardt, C., Fotakis, C., Vamvakaki, M. *et al.* (2011) 3D conducting nanostructures fabricated using direct laser writing. *Opt. Mater. Express*, **1**, 586–597.
- 91 Vasilantonakis, N., Terzaki, K., Sakellari, I., Purlys, V., Gray, D., Soukoulis, C.M. *et al.* (2012) Three-dimensional metallic photonic crystals with optical bandgaps. *Adv. Mater.*, **24**, 1101–1105.
- 92 Kenanakis, G., Xomalis, A., Selimis, A., Vamvakaki, M., Farsari, M., Kafesaki, M. *et al.* (2015) A three-dimensional infra-red metamaterial with asymmetric transmission. *ACS Photonics*, **2**, 287–294.
- 93 Soukoulis, C.M. and Wegener, M. (2011) Past achievements and future challenges in the development of three-dimensional photonic metamaterials. *Nat. Photonics*, **5**, 523–530.
- 94 Cao, Y.Y., Dong, X.Z., Takeyasu, N., Tanaka, T., Zhao, Z.S., Duan, X.M. *et al.* (2009) Morphology and size dependence of silver microstructures in fatty salts-assisted multiphoton photoreduction microfabrication. *Appl. Phys. A*, **96**, 453–458.
- 95 Cao, Y.Y., Takeyasu, N., Tanaka, T., Duan, X.M., and Kawata, S. (2009) 3D metallic nanostructure fabrication by surfactant-assisted multiphoton-induced reduction. *Small*, **5**, 1144–1148.
- 96 Lin, S.Y., Moreno, J., and Fleming, J.G. (2003) Three-dimensional photonic-crystal emitter for thermal photovoltaic power generation. *Appl. Phys. Lett.*, **83**, 380–382.
- 97 Lin, S.Y., Fleming, J.G., and El-Kady, I. (2003) Three-dimensional photonic-crystal emission through thermal excitation. *Opt. Lett.*, **28**, 1909–1911.
- 98 Fleming, J.G., Lin, S.Y., El-Kady, I., Biswas, R., and Ho, K.M. (2002) All metallic three-dimensional photonic crystals with a large infrared band-gap. *Nature*, **417**, 52–55.
- 99 Gansel, J.K., Latzel, M., Frolich, A., Kaschke, J., Thiel, M., and Wegener, M. (2012) Tapered gold-helix metamaterials as improved circular polarizers. *Appl. Phys. Lett.*, **100**, 101109.
- 100 Gansel, J.K., Thiel, M., Rill, M.S., Decker, M., Bade, K., Saile, V. *et al.* (2009) Gold helix photonic metamaterial as broadband circular polarizer. *Science*, **325**, 1513–1515.
- 101 Chen, Y.-S., Tal, A., Torrance, D.B., and Kuebler, S.M. (2006) Fabrication and characterization of three-dimensional silver-coated polymeric microstructures. *Adv. Funct. Mater.*, **16**, 1739–1744.

- 102 Radke, A., Gissibl, T., Klotzbücher, T., Braun, P.V., and Giessen, H. (2011) Three-dimensional bichiral plasmonic crystals fabricated by direct laser writing and electroless silver plating. *Adv. Mater.*, **23**, 3018–3021.
- 103 Hrapovic, S., Liu, Y.L., Enright, G., Bensebaa, F., and Luong, J.H.T. (2003) New strategy for preparing thin gold films on modified glass surfaces by electroless deposition. *Langmuir*, **19**, 3958–3965.
- 104 Mallory, G.O. and Hajdu, J.B. (eds) (1990) *Electroless Plating: Fundamentals and Applications*, American Electroplaters and Surface Finishers Society, Orlando, FL.
- 105 Rill, M.S., Plet, C., Thiel, M., Staude, I., Von Freymann, G., Linden, S. *et al.* (2008) Photonic metamaterials by direct laser writing and silver chemical vapour deposition. *Nat. Mater.*, **7**, 543–546.
- 106 Kavanagh, A., Copperwhite, R., Oubaha, M., Owens, J., McDonagh, C., Diamond, D. *et al.* (2011) Photo-patternable hybrid ionogels for electrochromic applications. *J. Mater. Chem.*, **21**, 8687–8693.
- 107 Oubaha, M., Kavanagh, A., Gorin, A., Bickaускаite, G., Byrne, R., Farsari, M. *et al.* (2012) Graphene-doped photo-patternable ionogels: Tuning of conductivity and mechanical stability of 3D microstructures. *J. Mater. Chem.*, **22**, 10552–10559.
- 108 Narayan, R. and Goering, P. (2011) Laser micro- and nanofabrication of biomaterials. *MRS Bull.*, **36**, 973–982.
- 109 Waldbaur, A., Rapp, H., Lange, K., and Rapp, B.E. (2011) Let there be chip-towards rapid prototyping of microfluidic devices: One-step manufacturing processes. *Anal. Methods*, **3**, 2681–2716.
- 110 Amato, L., Gu, Y., Bellini, N., Eaton, S.M., Cerullo, G., and Osellame, R. (2012) Integrated three-dimensional filter separates nanoscale from microscale elements in a microfluidic chip. *Lab Chip*, **12**, 1135–1142.
- 111 Eaton, S.M., De Marco, C., Martinez-Vazquez, R., Ramponi, R., Turri, S., Cerullo, G. *et al.* (2012) Femtosecond laser microstructuring for polymeric lab-on-chips. *J. Biophotonics*, **5**, 687–702.
- 112 Schizas, C., Melissinaki, V., Gaidukeviciute, A., Reinhardt, C., Ohrt, C., Dedoussis, V. *et al.* (2010) On the design and fabrication by two-photon polymerization of a readily assembled micro-valve. *Int. J. Adv. Manufact. Technol.*, **48**, 435–441.
- 113 Lin, C.L., Wang, I., Dollet, B., and Baldeck, P.L. (2006) Velocimetry microsensors driven by linearly polarized optical tweezers. *Opt. Lett.*, **31**, 329–331.
- 114 Maruo, S., Hasegawa, T., and Yoshimura, N. (2009) Replication of three-dimensional rotary micromechanism by membrane-assisted transfer molding. *Jpn. J. Appl. Phys.*, **48**, 06fh05.
- 115 Lee, J.T., George, M.C., Moore, J.S., and Braun, P.V. (2009) Multiphoton writing of three-dimensional fluidic channels within a porous matrix. *J. Am. Chem. Soc.*, **131**, 11294–11295.
- 116 Lin, C.L., Vitrant, G., Bouriau, M., Casalegno, R., and Baldeck, P.L. (2011) Optically driven Archimedes micro-screws for micropump application. *Opt. Express*, **19**, 8267–8276.
- 117 Gittard, S.D., Miller, P.R., Boehm, R.D., Ovsianikov, A., Chichkov, B.N., Heiser, J. *et al.* (2011) Multiphoton microscopy of transdermal quantum dot

- delivery using two photon polymerization-fabricated polymer microneedles. *Faraday Discuss.*, **149**, 171–185.
- 118 Gittard, S.D., Narayan, R.J., Jin, C., Ovsianikov, A., Chichkov, B.N., Monteiro-Riviere, N.A. *et al.* (2009) Pulsed laser deposition of antimicrobial silver coating on Ormocer (R) microneedles. *Biofabrication*, **1**, 041001.
 - 119 Gittard, S.D., Ovsianikov, A., Akar, H., Chichkov, B., Monteiro-Riviere, N.A., Stafslie, S. *et al.* (2010) Two photon polymerization-micromolding of polyethylene glycol-gentamicin sulfate microneedles. *Adv. Eng. Mater.*, **12**, B77–B82.
 - 120 Chatzinikolaïdou, M., Rekstyte, S., Danilevicius, P., Pontikoglou, C., Papadaki, H., Farsari, M. *et al.* (2015) Adhesion and growth of human bone marrow mesenchymal stem cells on precise-geometry 3D organic–inorganic composite scaffolds for bone repair. *Mater. Sci. Eng., C*, **48**, 301–309.
 - 121 Danilevicius, P., Rezende, R.A., Pereira, F., Selimis, A., Kasyanov, V., Noritomi, P.Y. *et al.* (2015) Burr-like, laser-made 3D microscaffolds for tissue spheroid encagement. *Biointerphases*, **10**, 021011.
 - 122 Langer, R. and Vacanti, J.P. (1993) Tissue Engineering. *Science*, **260**, 920–926.
 - 123 Zhang, S.G., Gelain, F., and Zhao, X.J. (2005) Designer self-assembling peptide nanofiber scaffolds for 3D tissue cell cultures. *Semin. Cancer Biol.*, **15**, 413–420.
 - 124 Abbott, A. (2003) Cell culture: Biology's new dimension. *Nature*, **424**, 870–872.
 - 125 Stratakis, E., Ranella, A., Farsari, M., and Fotakis, C. (2009) Laser-based micro/nanoengineering for biological applications. *Prog. Quantum Electron.*, **33**, 127–163.
 - 126 Dawood, F., Qin, S.J., Li, L.J., Lin, E.Y., and Fourkas, J.T. (2012) Simultaneous microscale optical manipulation, fabrication and immobilisation in aqueous media. *Chem. Sci.*, **3**, 2449–2456.
 - 127 Raimondi, M.T., Eaton, S.M., Nava, M.M., Laganà, M., Cerullo, G., and Osellame, R. (2012) Two-photon laser polymerization: From fundamentals to biomedical application in tissue engineering and regenerative medicine. *J. Appl. Biomater. Funct. Mater.*, **10**, 56–66.
 - 128 Ovsianikov, A., Mironov, V., Stampfl, J., and Liska, R. (2012) Engineering 3D cell-culture matrices: Multiphoton processing technologies for biological and tissue engineering applications. *Expert Rev. Med. Devices*, **9**, 613–633.
 - 129 Psycharakis, S., Tosca, A., Melissinaki, V., Giakoumaki, A., and Ranella, A. (2011) Tailor-made three-dimensional hybrid scaffolds for cell cultures. *Biomed. Mater.*, **6**, 16.
 - 130 Malinauskas, M., Danilevicius, P., Baltriukiene, D., Rutkauskas, M., Zukauskas, A., Kairyte, Z. *et al.* (2010) 3D artificial polymeric scaffolds for stem cell growth fabricated by femtosecond laser. *Lith. J. Phys.*, **50**, 75–82.
 - 131 Klein, F., Richter, B., Striebel, T., Franz, C.M., von Freymann, G., Wegener, M. *et al.* (2011) Two-component polymer scaffolds for controlled three-dimensional cell culture. *Adv. Mater.*, **23**, 1341–1345.

- 132 Tayalia, P., Mendonca, C.R., Baldacchini, T., Mooney, D.J., and Mazur, E. (2008) 3D cell-migration studies using two-photon engineered polymer scaffolds. *Adv. Mater.*, **20**, 4494–4498.
- 133 Raimondi, M.T., Eaton, S.M., Laganà, M., Aprile, V., Nava, M.M., Cerullo, G. *et al.* (2013) Three-dimensional structural niches engineered via two-photon laser polymerization promote stem cell homing. *Acta Biomater.*, **9**, 4579–4584.
- 134 Terzaki, K., Kissamitaki, M., Skarmoutsou, A., Fotakis, C., Charitidis, C., Farsari, M. *et al.* (2013) Pre-osteoblastic cell response on three-dimensional, organic–inorganic hybrid material scaffolds for bone tissue engineering. *J. Biomed. Mater. Res., Part A*. **101A**, 2283–2294.
- 135 Danilevicius, P., Georgiadi, L., Pateman, C.J., Claeysens, F., Chatzinikolaidou, M., and Farsari, M. (2015) The effect of porosity on cell ingrowth into accurately defined, laser-made, polylactide-based 3D scaffolds. *Appl. Surf. Sci.*, **336**, 2–10.
- 136 Terzaki, K., Kalloudi, E., Mossou, E., Mitchell, E.P., Forsyth, V.T., Rosseeva, E. *et al.* (2013) Mineralized self-assembled peptides on 3D laser-made scaffolds: A new route toward 'scaffold on scaffold' hard tissue engineering. *Biofabrication*, **5**, 045002.
- 137 Skarmoutsou, A., Lolas, G., Charitidis, C.A., Chatzinikolaidou, M., Vamvakaki, M., and Farsari, M. (2013) Nanomechanical properties of hybrid coatings for bone tissue engineering. *J. Mech. Behav. Biomed. Mater.*, **25**, 48–62.
- 138 Mačiulaitis, J., Deveikytė, M., Rekšytė, S., Bratchikov, M., Darinskas, A., Šimbelytė, A. *et al.* (2015) Preclinical study of SZ2080 material 3D microstructured scaffolds for cartilage tissue engineering made by femtosecond direct laser writing lithography. *Biofabrication*, **7**, 015015.
- 139 Engelhardt, S., Hoch, E., Borchers, K., Meyer, W., Kruger, H., Tovar, G. *et al.* (2011) Fabrication of 2D protein microstructures and 3D polymer–protein hybrid microstructures by two-photon polymerization. *Biofabrication*, **3**, 3025003.
- 140 Turunen, S., Kämpylä, E., Terzaki, K., Viitanen, J., Fotakis, C., Kellomäki, M. *et al.* (2011) Pico- and femtosecond laser-induced crosslinking of protein microstructures: Evaluation of processability and bioactivity. *Biofabrication*, **3**, 045002.
- 141 Ovsianikov, A., Malinauskas, M., Schlie, S., Chichkov, B., Gittard, S., Narayan, R. *et al.* (2011) Three-dimensional laser micro- and nano-structuring of acrylated poly(ethylene glycol) materials and evaluation of their cytotoxicity for tissue engineering applications. *Acta Biomater.*, **7**, 967–974.

6

High Speed Sintering: The Next Generation of Manufacturing

Adam Ellis

6.1 The Need for the Next Generation of Additive Manufacturing

A report written in 2012 by a special interest group on behalf of the UK Technology Strategy Board (now Innovate UK), entitled “Shaping Our National Competency in Additive Manufacturing,” indicated that industries require processes that are 4–10× faster. In addition to the speed improvement, cost reduction properties and accuracy were identified as areas that must be addressed. Currently, the leading technology is laser sintering (LS). This is a well-established technology, but lasers are expensive and inefficient to move around a powder bed surface. This inefficiency of movement implies an undesirable processing speed, which in turn leads to a high part cost.

If additive manufacturing is to be brought into the realms of high volume or mass manufacture, an analysis of what volumes are economically viable must be considered. Current Additive Manufacturing (AM) technologies are not capable of producing high-volume products such as fast-moving consumer goods. AM has been accepted in niche applications; currently, AM technologies are producing low-volume high-added-value products in the aerospace and automotive sectors. AM has begun to break away from niche into personalized footwear, and New Balance currently furnish their elite athletes with laser-sintered running shoe soles tailored to the athletes specific needs and running style.

Accuracy, detail, and surface finish are all disadvantages of AM compared with other manufacturing processes. Consequently, these issues have received a great amount of research and witnessed significant improvements. However, in many aesthetic applications, postprocessing, which could offset any benefits of AM, may be required, leading to the use of alternative traditional approaches. For many nonvisible parts, such as under-the-bonnet applications, surface finish is less of an issue and AM may be more suitable. To break into the mainstream, the problem of speed and cost of AM must be addressed.

A cost analysis by Hopkinson and Dickens is shown in Figure 6.1. The analysis is based on a complex thumb-sized part and shows the cost per part versus the production volume [1].

In the graph shown in Figure 6.1, the curved line represents the cost per part for injection molding, tooling costs are amortized as the production volume rises,

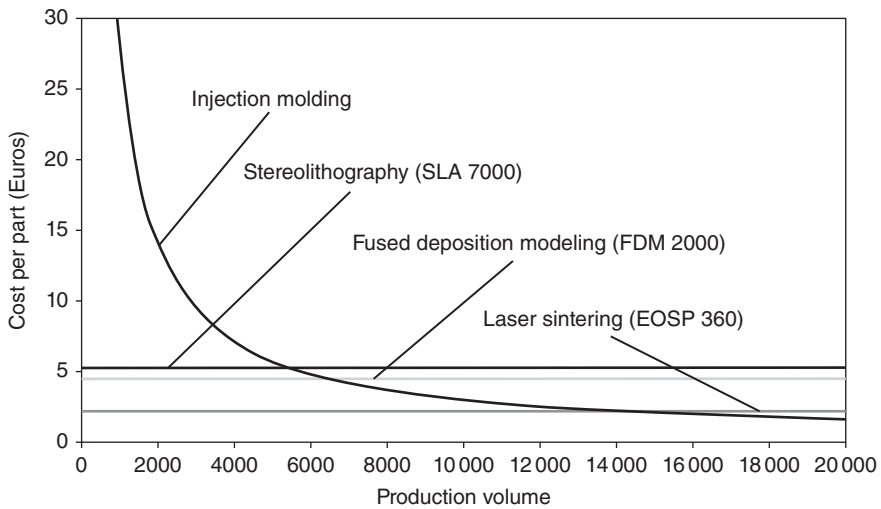


Figure 6.1 A cost analysis of injection molding versus various additive manufacturing technologies.

and the cost of the part is therefore reduced at high production volume. The three horizontal lines represent stereolithography, fused deposition modeling, and LS from top to bottom, respectively. Stereolithography was invented and patented by Chuck W. Hull in 1986 [2]. The process involves UV-initiated polymerization of a curable resin. A UV laser is used to scan a predetermined cross-sectional area of a vat of resin to create a solid layer, and this process is then repeated until the part(s) are complete. This process has been used to manufacture a wide array of parts including polymeric and microstructures and a variety of parts used in biomedical engineering [3, 4]. Fused deposition modeling is based on the molten extrusion of typically a polymer filament onto a surface upon which it quickly solidifies. The nozzle follows a path defined by the CAD model to build up the part. In Laser Sintering, a layer of powder is deposited, and a high powered laser is used to sinter the desired cross section. A new layer of powder is deposited, and the process is repeated until the part is complete [5].

In each case, the point at which the horizontal line for each AM process crosses the curved line from injection molding represents the production volume at which it becomes cheaper to manufacture the part using injection molding. This is around 5000 for stereolithography and 7000 for fused deposition modeling; this shows that layer manufacturing methods are more economical than traditional approaches for production of thousands of units. The cross-over production volume for LS was 14 000. Although a handful of large LS bureaus are producing this production volume, it requires large number of machines at significant cost. Today's AM technologies are not able to produce this volume of parts economically. To bring the benefits of additive manufacturing to mass production and compete with injection molding, the cutoff point must be

increased to higher volumes, hundreds of thousands or millions of units. To do this, machine cost and speed must be addressed.

6.2 High Speed Sintering

High speed sintering (HSS) is a novel powder-based additive manufacturing technology intended to maintain the attractive features of LS while addressing the drawbacks such as machine cost and process speed. The process operates layer-by-layer in which the layer of powder is deposited, an inkjet printhead then deposits a radiation absorbing material (RAM) onto the desired area, and an infrared lamp then irradiates the entire surface. Many examples of sintering metal or metal nanoparticles using inkjet printing and IR exposure exist in the literature. These include sintering metals onto a paper substrate and using a silver-containing ink to create sintered conductive pathways [6–10]. In HSS, the printed area absorbs sufficient energy to elevate the temperature of the powder to its melt point, allowing sintering to take place. Areas not printed with the RAM will absorb less energy, therefore, not exceeding their melt point and not becoming sintered. This approach allows each layer to be sintered in one pass; therefore, the layer time is independent of the part geometry. The unsintered powder can be brushed away from the part on completion of the build (Figure 6.2).

6.3 Machine Setup & Parameter Control

The HSS process may be broken down into a number of distinct steps required for each build. As for many AM technologies, the first step is the production of the CAD model. This CAD model is then digitally sliced into 2D cross sections,



Figure 6.2 Parts manufactured by high speed sintering. (Image courtesy of Xaar.)

each of which represents one layer. The powder and the machine itself must also be prepared; the machine contains two beds, one of which is the build bed where the parts are manufactured and the other is the feed bed, which stores and heats the feed powder. A counter-rotating roller transfers material from the feed bed to the build bed. The feed bed is raised to sit proud of the build surface and the build bed lowered to receive the transfer of powder. The build bed is loaded with around 10 mm depth of powder prior to the manufacture of parts. Both beds are heated from all sides by a heating jacket and overhead heaters. The temperature of the build bed is maintained slightly below the melt temperature of the powder. The powder in the feed bed is maintained at a lower temperature so that the powder is preheated to a point that assists with fast and reliable production but becomes too high as this can inhibit powder deposition. Moreover, it is necessary to elevate the temperature of the feed powder so comparatively cold powder is not deposited onto the hot surface of the build bed. Once the powder has been allowed to reach the desired temperature, the build may begin. The first operation is to deposit a layer of powder, then RAM is deposited onto the powder surface, and an IR lamp causes the printed area to sinter. An image of the first custom-built high-speed machine taken during a build is shown in Figure 6.3.

Unlike LS, HSS does not require an inert atmosphere. Early experiments performed at Loughborough University (UK) showed that an inert atmosphere was not required and that part quality and performance was not influenced heavily by the presence of ambient oxygen.

For polymer-based processes, the thermal behavior of the powder is pivotal. Differential scanning calorimetry (DSC) may be used to determine the melting and recrystallization temperatures for a material and will indicate whether the polymer possesses supercooling behavior; that is, the melting temperature is higher than that of the recrystallization temperature. The current industry standard for HSS and LS is Nylon 12, the DSC analysis is shown in Figure 6.4.

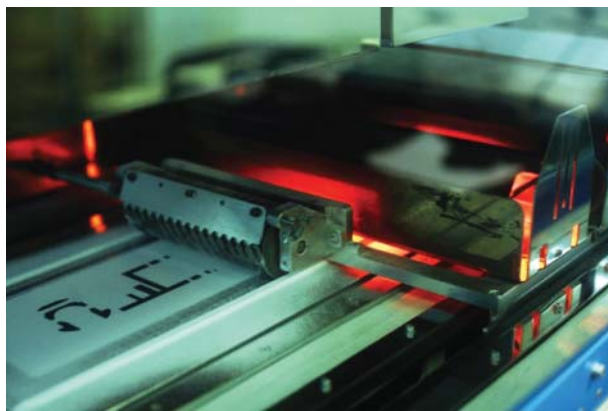


Figure 6.3 High speed sintering in action, the black image on the white powder provides the selectivity crucial to the process.

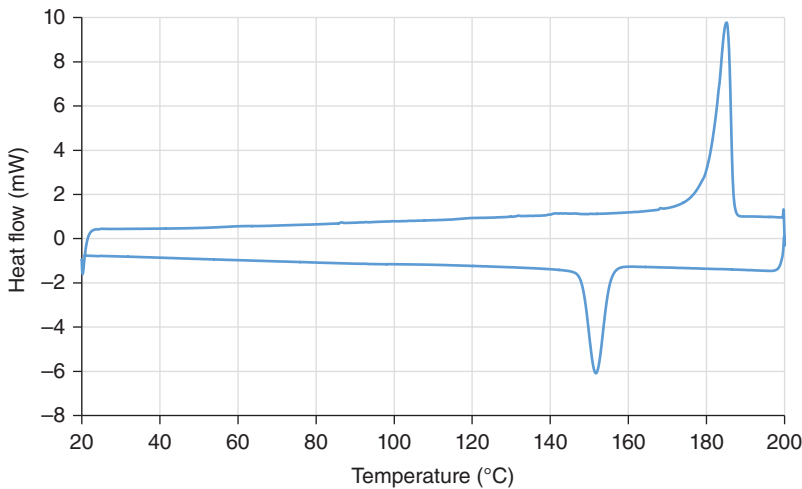


Figure 6.4 DSC analysis showing the supercooling behavior of Nylon 12.

Supercooling is preferable as it allows the part to be maintained above recrystallization subsequent to sintering. This behavior is apparent in Figure 6.4 with a melt onset temperature of $\sim 173^{\circ}\text{C}$ and a recrystallization onset temperature of $\sim 159^{\circ}\text{C}$. This is crucial as rapid cooling, and, therefore, solidification induces thermal stresses and causes the part to curl causing the build to fail. A large sintering region is therefore preferred, with any overlap in the melt and recrystallization temperature ranges giving a lower thermal tolerance. Vasquez *et al.* have identified the stable sintering region for LS. As the material requirements for HSS are very similar to that of LS, this is transferable. However, in the case of HSS, the short layer time reduces the likelihood of curling induced by overcooling of sintered material and thus materials with smaller supercooling process windows, such as nylon 11, are more reliably processed in HSS than in LS. The stable sintering region describes the optimum sintering region for successful sintering. This is the region that lies between the temperature at which the material is able to flow measured by DSC and 1% weight loss measured by TGA [11].

To avoid curling, which is induced by excessive cooling, it is crucial that, once sintered, the parts remain above the temperature of recrystallization. To ensure that each layer of freshly deposited powder does not cause the layer underneath to cool down to the recrystallization temperature, the feed powder is maintained at an elevated temperature. The preheat lamp is employed to impart extra energy to the powder immediately after it has been deposited for the same reason. The sintering stroke irradiates the entire build surface with IR energy causing only areas deposited with RAM to sinter. It is possible to fine-tune the amount of energy imparted to the build surface by adjusting the speed of travel and the lamp power.

Alongside this parameter control, the volume of ink deposited on the build surface may also be controlled. The amount of RAM on the surface will strongly influence the amount of energy transferred to the underlying powder. The volume of ink deposited is controlled by grayscale, which has a range of 0–255, where 0



Figure 6.5 Continuous grayscale from 0 at the extreme left to 255 at the extreme right.

represents black and 255 represents white. Thus, the lower the number, the more ink is printed onto the powder surface. An example is shown in Figure 6.5.

Control of parameters is critical to optimize mechanical performance, which includes the set temperatures and the grayscale at which the RAM will be deposited. Various studies have shown the influence of parameter control on the microstructure and mechanical properties of HSS parts. The lamp power has been shown to influence sintering behavior [12]. Majewski *et al.* also showed that increasing bed temperature and infrared lamp power increased Young's modulus, tensile strength, and elongation at break. This effect must be used with caution as the increase in mechanical performance was at the cost of powder removal [13].

Work by Ellis *et al.* has shown that the amount of ink deposited on the surface influences the degree of particle melt and mechanical performance. Results showed that the microstructure of the part was influenced by the print density, with crystallinity decreasing as print density increased. Mechanical properties were also influenced as print density increased; stiffness and tensile strength increased with crystallinity at the expense of ductility. This work also showed that despite the presence of RAM in the final part, HSS parts showed a similar crystallinity to laser-sintered parts, indicating that RAM has minimal effect on microstructure and crystallinity [14].

Print density has also been shown to influence part density due to the amount of RAM having a significant effect on the properties of high speed sintered parts. The degree of particle melt at these parameters is complete around GS 142, which is also the peak of mechanical performance [15].

6.4 Materials & Properties

As is currently the case for LS, HSS uses Nylon 12 as standard with a layer thickness of 100 μm . This layer thickness typically uses powder with a D50 of $\sim 50 \mu\text{m}$ and a D90 of $\sim 90 \mu\text{m}$. This ensures that the majority of particles are under 100 μm , which will allow for a uniform layer to be deposited without any particles protruding from the surface, which may interfere with powder deposition or indeed contact the printhead upon ink deposition. When parts are built using Nylon 12, HSS is able to achieve values equal to or above LS as shown in Table 6.1, the LS data were taken from an OEM datasheet.

The data shows that HSS is able to compete with LS for tensile strength but offers a marked improvement in elongation at break. This is discussed in more detail shortly. As the material requirements are similar, HSS has successfully processed many LS-grade polymeric powders; indeed, it is expected that due to a much faster layer time HSS may be able to process polymers that LS cannot.

Table 6.1 Mechanical data for high speed sintering, cf. laser sintering.

	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Laser sintering	43	14	1600
High speed sintering	45	22	1700

With TPE 210-S manufactured by ALM, HSS was able to achieve elongation at break up to 365% compared with 110% for LS [16]. It is believed that this profound difference is due to the nature of the HSS mechanism, depositing ink, and sintering with infrared rather than scanning with a laser. Haworth *et al.* have shown that polymers incur slow sintering times, and Frenkel model predictions based on surface energy data show that sintering time depends on the thermal history of the powder in use [17]. Virgin powder has a sintering time of around 1 s; the sintering time gradually increases with the percentage content of used powder in the feed material reaching maximum of approximately 7 s for 100% used powder.

Therefore, the sintering time is in the order of seconds; however, for LS the laser interaction time is very short, typically one ten thousandth of the sintering time [18]. For viscous polymers such as elastomers, the sintering time is increased substantially, implying that the laser interaction time is even lower compared to the sintering time, whereas in HSS the infrared exposure time is in the order of a second, orders of magnitude higher than the laser interaction time. This represents a significant advantage of HSS for viscous materials such as elastomers and offers an explanation for the significant increase in mechanical performance.

The difference in exposure time relative to the sintering time is attributed to the existence of poor surface finish in LS. It is well known that powder that has been recycled from the part cake of previous builds in LS will lead to poor surface finish, known as orange peel. Anecdotal evidence suggests that this can be minimized by altering machine parameters to increase the laser interaction time by methods such as double scanning. Despite such mitigation, orange peel and thus poor surface finish remain a problem for used powder in LS.

Possibly due to the elongated exposure time, the orange peel effect has never been observed in HSS. Powder may be reused an unlimited number of times without detriment to surface finish. As material costs dominate the price of parts, this is a significant advantage and allows the cost per part to be reduced substantially.

6.5 HSS for High-Volume Manufacturing

A key aspect of high speed sintering is scalability. While LS machines exist with twin lasers, large beds incur extended layer times. A HSS machine with a large build area would be possible by using an array of printheads to produce a wide

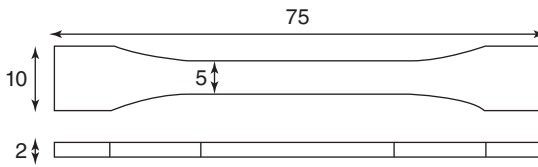


Figure 6.6 The tensile test specimen used for the build projection (dimensions in mm).

print swathe coupled with one single or multiple infrared lamps to span the build width.

The scalability may be exemplified by a build time projection for a large machine with a build volume of $1\text{ m} \times 1\text{ m} \times 1\text{ m}$ that is capable of depositing powder, printing, and sintering bidirectionally based on a tensile test specimen shown in Figure 6.6.

Assuming as follows:

- Warm up/cool down for total of 3 h
- Layer cycle time of 20 s
- Allow a 2 mm gap between parts in all directions
- Allow a 10 mm gap around the edge and top/bottom of build bed.

This would allow the following:

- Parts per level = 1250
- No. of levels = 247
- Parts per build = 308 750.

With a build time of

- $20\text{ s} \times 9800$ (no of layers) + 3 h
- 206 800 s
- 0.67 s per part.

This build project for a large machine is based on a layer time of 20 s, which is a reasonable target for a machine of this size. At this layer time, a tensile test specimen of this size shown earlier would be manufactured with an average time of 0.67 s. Moreover, a cost based on Ruffo model estimates this part to be manufactured at a cost of £0.13 [19]. This represents a step change in additive manufacturing and presents HSS as a genuine option for high-volume manufacture.

With the capability to manufacture parts in less than 1 s, without the need for tooling, HSS will allow additive manufacturing to break away from niche applications. Today's typical applications are low-volume high-added-value products in automotive and aerospace. The speed and low cost of HSS will displace a small but significant amount of the injection molding market.

Opportunities for high-volume AM are emerging in many sectors including consumer products. Consumer demands are currently unmet; customization, performance, design freedom, and cost all play a role. Manufacturing flexibility, responsiveness, and reduced environmental impact are powerful driving forces for the acceptance of AM into the mainstream.

Figure 6.7 Customized shoe soles manufactured by high speed sintering.



6.6 Case Study: From Elite to High Street

An example of the ability of AM to push into the mainstream was a research project entitled “Elite to High Street”, funded with over £1M from Loughborough University’s EPSRC-funded Innovative Manufacturing and Construction Research Centre (IMCRC). The goal of this project was to manufacture personalized athletic footwear at point of purchase on the high street and to manufacture personalized athletic footwear from elite athletes (Figure 6.7).

This project manufactured intricate shoe sole designs that were hitherto impossible to create a range of longitudinal bending stiffness that delivered enhanced performance. It is expected that this type of personalized customization will be available on the high street for consumer footwear subject to an open supply chain and a further reduction in part cost.

6.7 Opening the Supply Chain

In an effort to open the supply chain, Factum (2014-2017), a £1.5M project funded by Innovate UK aimed to develop supply chain and full-scale production capabilities for novel additive manufacturing technologies based on LS and HSS for application in three major industrial sectors within the UK economy (Figure 6.8). The three sectors are each represented by project partners:



Figure 6.8 The Factum project logo.

Unilever (fast-moving consumer goods); BAE Systems (aerospace); and Cobham Technical Services (space and communication).

High speed sintering manufacturing capability was developed and exploited by the consortium partners that composed, in addition to end-users, manufacturing machine capability developers (Xaar), product design specialty (Sebastian Conran Associates), and polymer processing and additive manufacturing specialists (FaraPack Polymers Ltd) based at the University of Sheffield. Factum aimed to initiate a validated supply chain by creating suitable demonstrator products in three industry sectors and an appropriate exploitation plan for effective commercialization of LS and HSS products.

6.8 The Future of HSS and the Benefits of Inkjet

The presence of inkjet technology presents a vast number of opportunities for HSS. This allows the opportunity to tailor the performance of parts by selecting an appropriate RAM or ink and manufacture parts with added functionality. An obvious choice would be the introduction of color. If full color inkjet could be combined with the required thermal performance of the ink, this would open up the opportunity to manufacture parts with a rainbow of colors all from the same starting material. Other additives would also be possible, such as flame retardants and other materials to increase the mechanical performance such as nanofiller materials or carbon nanotubes.

An exciting possibility is the *in situ* introduction of electrically conductive pathways into parts. A £1M project funded by the EPSRC to produce an HSS machine with a build bed of 1.6 m × 0.8 m × 0.075 m began in April 2015 and is scheduled for completion in early 2017. This machine is expected to contain two printhead arrays, one of which will deposit RAM and cause sintering and the other will be used to deposit functional materials, such as metal nanoparticles for electrically conductive pathways. This would represent a real step change in production and allow electronically functional parts to be produced in ways that are currently out of reach for traditional manufacturing approaches.

Material recycling, speed, part performance, accuracy, and cost render HSS a genuine high-volume manufacturing technology. With speeds capable of competing with injection molding, HSS will undoubtedly disrupt the existing manufacturing zeitgeist and HSS has the potential to transform the future of manufacturing.

References

- 1 Hopkinson, N. and Dickens, P. (2003) Analysis of rapid manufacturing—using layer manufacturing processes for production. *Proc. Inst. Mech. Eng., Part A*, **217** (1), 31–39.
- 2 Hull, C.W. (1986) Apparatus for production of three-dimensional objects by stereolithography, US 4575330 A, Google Patents.

- 3 Zhang, X., Jiang, X., and Sun, C. (1999) Micro-stereolithography of polymeric and ceramic microstructures. *Sens. Actuators, A*, **77** (2), 149–156.
- 4 Melchels, F.P., Feijen, J., and Grijpma, D.W. (2010) A review on stereolithography and its applications in biomedical engineering. *Biomaterials*, **31** (24), 6121–6130.
- 5 Goodridge, R.D., Tuck, C.J., and Hague, R.J.M. (2012) Laser sintering of polyamides and other polymers. *Prog. Mater. Sci.*, **57** (2), 229–267.
- 6 Cherrington, M., Claypole, T.C., Deganello, D., Mabbett, I., Watson, T., and Worsley, D. (2011) Ultrafast near-infrared sintering of a slot-die coated nano-silver conducting ink. *J. Mater. Chem.*, **21** (21), 7562–7564.
- 7 Denneulin, A., Blayo, A., Neuman, C., and Bras, J. (2011) Infra-red assisted sintering of inkjet printed silver tracks on paper substrates. *J. Nanopart. Res.*, **13** (9), 3815–3823.
- 8 Määttänen, A., Ihalainen, P., Pulkkinen, P., Wang, S., Tenhu, H., and Peltonen, J. (2012) Inkjet-printed gold electrodes on paper: Characterization and functionalization. *ACS Appl. Mater. Interfaces*, **4** (2), 955–964.
- 9 Tobjörk, D., Aarnio, H., Pulkkinen, P., Bollström, R., Määttänen, A., Ihalainen, P., Mäkelä, T., Peltonen, J., Toivakka, M., Tenhu, H., and Österbacka, R. (2012) IR-sintering of ink-jet printed metal-nanoparticles on paper. *Thin Solid Films*, **520** (7), 2949–2955.
- 10 Wunscher, S., Abbel, R., Perelaer, J., and Schubert, U.S. (2014) Progress of alternative sintering approaches of inkjet-printed metal inks and their application for manufacturing of flexible electronic devices. *J. Mater. Chem. C*, **2** (48), 10232–10261.
- 11 Vasquez, M., Haworth, B., and Hopkinson, N. (2013) Methods for quantifying the stable sintering region in laser sintered polyamide-12. *Polym. Eng. Sci.*, **53** (6), 1230–1240.
- 12 Majewski, C.E., Oduye, D., Thomas, H., and Hopkinson, N. (2008) Effect of infra-red power level on the sintering behaviour in the high speed sintering process. *Rapid Prototyping J.*, **14** (3), 155–160.
- 13 Majewski, C.E., Hobbs, B.S., and Hopkinson, N. (2007) Effect of bed temperature and infra-red lamp power on the mechanical properties of parts produced using high speed sintering. *Virtual Phys. Prototyping*, **2** (2), 103–110.
- 14 Ellis, A., Noble, C.J., and Hopkinson, N. (2014) High Speed Sintering: Assessing the influence of print density on microstructure and mechanical properties of nylon parts. *Addit. Manuf.*, **1–4**, 48–51.
- 15 Noble, C.J., Ellis, A., and Hopkinson, N. (2014) Effect of greyscale/print density on the properties of high speed sintered nylon 12, in *Solid Freeform Fabrication Symposium*, University of Texas, Austin, USA, pp. 132–142.
- 16 Ellis, A., Noble, C.J., Hartley, L., Lestranger, C., Hopkinson, N., and Majewski, C. (2014) Materials for high speed sintering. *J. Mater. Res.*, **29** (17), 2080–2085.

- 17 Haworth, B., Hopkinson, N., Hitt, D., and Zhong, X. (2013) Shear viscosity measurements on Polyamide-12 polymers for laser sintering. *Rapid Prototyping J.*, **19** (1), 28–36.
- 18 Vasquez, G.M. (2012) *Analysis and development of new materials for polymer laser sintering*, Loughborough University, UK.
- 19 Ruffo, M., Tuck, C., and Hague, R. (2006) Cost estimation for rapid manufacturing-laser sintering production for low to medium volumes. *Proc. Inst. Mech. Eng., Part B*, **220** (9), 1417–1427.

7

Metallic Nanoinks for Inkjet Printing of Conductive 2D and 3D Structures

Alexander Kamyshny and Shlomo Magdassi

7.1 Introduction

During the last decade, the field of printed electronics, that is, application of printing technologies for the fabrication of conductive electronic devices on solid and flexible substrates, received a tremendous interest [1–12]. The market for printed electronics has been estimated to reach \$40.2 billion by 2020 [13].

Traditional methods of manufacturing electronic devices are photolithography, vacuum deposition, and electroless plating processes. These methods are multistage, require high-cost equipment, and involve the use of environmentally undesirable chemicals, which results in usually the formation of large amounts of waste.

A better alternative to these procedures is *screen printing* of conductive films using pastes containing metal micro- or nanoparticles (usually Ag or Ag alloys). This technique is very simple to operate, involves only two steps: printing and curing the obtained pattern and is compatible with a large variety of materials [2, 14, 15]. The obtained conductivities are usually compatible with conductivity of bulk metal [16–19]. The disadvantage of screen printing is its rather high cost due to the large amount of ink required relative to the yield.

A number of direct techniques for deposition of metallic inks, such as spin, spray, dip, and rod coating, as well as various printing methods such as flexo and gravure are also available [8]. Recently, a new filamentary printing method was reported, in which silver nanoink with high metal load (up to 85%) is extruded through a tapered cylindrical nozzle that is suitable for the fabrication of 3D structures. The printed feature dimensions are determined by the ink properties such as rheology and by the printing parameters. Using this approach, 2D and 3D conductive patterns can be printed [20–22].

Drop-on-demand inkjet printing, which is an additive, noncontact, fast, low-cost, and eco-friendly method, is of obvious advantage compared to most of the deposition methods [2, 8, 9, 23]. Inkjet printing was demonstrated to be a very effective technique for manufacturing various electronic devices such as circuit boards, RFID tags, thin-film transistors (TFTs), light-emitting devices, organic solar cells (OSCs), transparent conductive electrodes (TCEs), touch screens, flexible displays, electrochromic devices, and piezoelectric

actuators [1–7, 23–27]. In addition, inkjet printing is favorable for large-area manufacturing of flexible electronic devices by the roll-to-roll (R2R) technique [8, 9] and enables patterning with high resolution (line and space dimensions can be as small as 10–20 μm) [28, 29].

The conductive material may be dispersed metal nanoparticles (NPs) and nanowires (NWs), carbon nanotubes (CNTs), graphene sheets, conductive polymers (dissolved or dispersed) as well as organometallic compounds and complexes as precursors, which convert into metal upon postprinting treatment [1, 2, 26, 30, 31]. The selection of the conductive material is mainly determined by the required physical properties of the printed device such as conductivity, optical transparency, and stability of printed pattern to bending that is especially important for flexible substrates.

In this chapter, we focus on conductive inkjet inks based on metal NPs (metallic nanoinks), which are suitable for fabrication of 2D and 3D conductive structures. We describe methods for metal NP fabrication, mainly wet chemical methods, which enable large-scale production of uniform metal NPs for conductive inks, their stabilization against aggregation, and oxidation at ambient conditions. We also discuss the formulation of conductive inkjet inks, printing, and postprinting treatments of 2D and 3D patterns for obtaining high electrical conductivity. Several applications of metallic nanoinks in printed electronics are also presented.

7.2 Metallic Nanoinks: Requirements and Challenges

Besides the electrical properties of the printed patterns, the basic requirements for conductive inkjet inks are similar to those of conventional inkjet inks: good printability, matching the ink to the substrate (optimal wetting, spreading, and penetration) to provide high resolution, good adhesion to the substrate, and long shelf-life.

Therefore, as in graphic arts ink, conductive inkjet ink is a multicomponent system that contains a functional conducting material in a liquid vehicle (aqueous or organic) and various additives (such as rheology and surface tension modifiers, humectants, binders, and defoamers), which enable optimal performance of the whole system, including the printing device and the substrate [28, 29]. For example, thermal printheads require viscosity of ink to be below 3 cP, while for optimal performance of piezoelectric printheads, the ink viscosity should be in the range of 8–15 cP [28].

While using metal NPs as the functional component of inkjet ink, some specific requirements need to be met, and several specific challenges should be overcome for obtaining high-quality conductive patterns. As a general rule, the size of the particles in inkjet ink formulation should be about 0.01 of the diameter of the printhead's orifice (typically 20–50 μm) to avoid its clogging and blockage. However, the small size, 30–50 nm, is preferable [32, 33]. These particles should be stable against aggregation and precipitation at high metal loading, typically 20–60 wt% in commercial inks (the high metal loading is required for obtaining highly conductive printed patterns), in order to provide optimal performance.

To ensure the stability of metal NPs, the ink formulation should contain a stabilizing agent, which is usually a polymeric material or a surfactant [34]. The second challenge is the oxidation of NPs at ambient conditions, in case they are composed of nonnoble metals [1, 2, 35]. Replacement of noble metals such as silver, which is the most reported material for conductive inks, by nonnoble ones, is especially important for low-cost mass production of electronic devices. Successful utilization of such metals (e.g., Cu, Al, Ni) would depend on the success in avoiding their oxidation in ink composition and during the printing and postprinting processes, as is discussed later. One more challenge in using metallic nanoinks results from the need to sinter the metal particles in order to obtain continuous metallic patterns. This brings the need for effective postprinting processes in order to remove the stabilizer present on the particle's surface, which is actually an insulating organic material. Especially important is the development of nondestructive sintering processes, which can be applicable for R2R printing on heat-sensitive flexible substrates such as plastics and paper, to enable the fabrication of "plastic electronic devices" (the various methods of sintering are discussed later).

7.3 Synthesis and Stabilization of Metal NPs for Conductive Nanoinks

7.3.1 Synthesis

Two main approaches are used for the preparation of metal NPs: top-down and bottom-up.

In the top-down methods, NPs are formed by breaking bulk metal. These methods include mechanical grinding, laser ablation in a proper liquid, rapid condensation of metal vapors obtained by electroexplosion of a metal wire, thermal heating, or plasma excitation of metal plates, powders, or wires followed by the transport of formed NPs with a stream of an inert gas (N_2 and Ar) onto a solid substrate or into a proper liquid [36–43]. The main disadvantages of these methods are the difficulties in obtaining uniform NPs and their aggregation to polycrystalline powder as well as the high cost due to high energy consumption and need for sophisticated equipment.

In the bottom-up approach, metal NPs are formed from precursor ions by a reaction with a proper reducing agent in a liquid medium ("wet" chemical approach), which can vary from water to polar and nonpolar solvents and also ionic liquids [30, 37, 44–46], or by a decomposition of the precursor (salts and organometallic molecules [2, 47]). Organometallic compounds are able to decompose either spontaneously upon heating or in the presence of a reducing agent, for example, gaseous hydrogen. Organometallic compounds can be carbonyls, olefinic complexes, dibenzylidene acetates, acetyl acetates, or complexes of metals with fatty acids [2, 48–52].

Wet chemistry methods yield a great variety of dispersions with various particle characteristics such as size distribution, morphology, and stability toward aggregation and sedimentation. The control of these properties is achieved by varying

many experimental parameters of the reaction, such as concentration of reagents, redox potentials of the reducing agent, temperature, pH, and rate of reagent addition, addition of preformed seeds, type and concentration of protective agents [30, 53–57].

The first step in forming metal NPs in liquid from the corresponding ions is their reduction to metal atoms, and the reaction is possible only if the reduction potential of the reducing agent is more negative than the reduction potential of the metal precursor. Practically, the difference should be larger than 0.3–0.4 V; otherwise, the reaction may proceed too slowly to be of practical importance [58].

In aqueous medium, cations of strongly electropositive metals, such as Ag^+ ($E^0 = 0.8 \text{ V}$), Au^{3+} ($E^0 = 1.5 \text{ V}$), Pt^{2+} ($E^0 = 1.2 \text{ V}$), and Pd^{2+} ($E^0 = 0.99 \text{ V}$) [30, 59], can be reduced by relatively mild reducing agents. Cations of moderately electropositive metals, for example, Cu^{2+} ($E^0 = 0.34 \text{ V}$), require stronger reducing agents, while cations of electronegative metals, such as Ni^{2+} ($E^0 = -0.23 \text{ V}$) and Sn^{2+} ($E^0 = -0.14$) [59], can be reduced only by strong reducing agents, and the reaction proceeds usually at elevated temperatures [30, 60–65].

Among the reducing agents, the most often used are sodium borohydride (NaBH_4) and hydrazine (N_2H_4), which are more effective in alkaline medium ($E^0 = -1.24$ and -1.16 V , respectively), citrate ($E^0 = -0.56 \text{ V}$), and ascorbic acid [30]. The latter is a weak reducing agent effective only in reactions with ions of strongly electropositive metals. Such ions can also be reduced by organic compounds containing oxidizable hydroxyl and carbonyl groups (alcohols with α -hydrogen, aldehydes, and carbohydrates) and organic amines [30, 66]. Sodium phosphinate was also used as a reducing agent for the synthesis of metal NPs [67, 68].

Besides water, the solvents that are widely used for synthesis of metal NPs are polyols (ethylene glycol, propylene glycol, and diethylene glycol). They act both as solvents for the metal precursor and as reducing agents. The reactions can be performed at elevated temperatures, up to 250°C , at which finely dispersed NPs are usually produced. Since polyols are mild reducing agents, they are more suitable for the fabrication of NPs of electropositive metals, such as silver, gold, palladium, and platinum [44, 69, 70]. The polyol method is also widely used for the fabrication of silver and copper nanowires [71–74]. Among other organic solvents, toluene is also used as a solvent for the reduction of metal NPs precursors [75].

Reduction of metal ions with the formation of NPs can also be performed by electrolysis of a metal salts in solution [76, 77], as well as by sonochemical [78, 79] and sonoelectrochemical [80] methods. High energy radiations (UV-, γ -, and electron beam) are also applied to obtain dispersions of metal NPs [43, 81–83].

7.3.2 Stabilization

7.3.2.1 Stabilization Against Aggregation

One of the most crucial properties of the ink is the stability of the synthesized metal NPs in the ink formulations. Since the colloidal dispersion represents a state of higher free energy compared to bulk metal, aggregation followed by agglomeration and sedimentation tends to occur spontaneously. To prevent

agglomeration and coalescence and to obtain stable dispersions, the aggregation process must be prevented, and this is usually achieved by special additives. Selecting the proper stabilizer and the composition of the liquid vehicle of the ink are of great importance, since these components affect the shelf-life and the overall performance of the ink [1, 28, 29].

According to the classical DLVO theory, colloidal stability is determined by the balance between repulsive and attraction energies. Electrical repulsion energy is a function of surface electrical potential of the interacting particles, the medium permittivity, and the Debye–Hückel parameter, which determines the thickness of electrical double layer. The attraction (van der Waals) energy is inversely proportional to the distance between interacting particles, to the Hamaker constant, and to the diameter of the particles. In aqueous dispersions, the crucial condition for obtaining stable (or more correct, metastable) dispersions is the value of electrical potential: the higher this potential, the stronger the electrostatic repulsion between the interacting particles, and the more stable colloidal system [30, 84]. A measure of the surface electrical potential of a particle is the zeta potential (ζ), which refers to the potential at the boundary between the moving particle and the liquid. The dispersions of colloidal particles are considered to be stable at zeta potential of higher than 35–40 mV [30]. Electrostatic stabilization of metal NPs is usually achieved by adsorbed ionic surfactants. Typical examples are the cationic surfactant CTAB (cetyltrimethylammonium bromide) [85–87] and the anionic surfactants, such as SDS (sodium dodecyl sulfate) [88, 89], AOT (sodium bis(2-ethylhexyl)sulfosuccinate) [90], and sodium oleate [91].

Since the thickness of the electrical double layer decreases with the increase in ionic strength, the particles can contact each other closely, collide, and flocculate in dispersions having high electrolyte concentrations. Dispersions with high metal load, which is required for conductive ink formulations, contain high concentration of the metal ions during the synthesis step. This would obviously lead to aggregation of the metal NPs already at this step. To overcome this disadvantage of electrostatic stabilization, steric stabilization of metal NPs is frequently used. It is achieved by surrounding the particles with a layer of sterically bulky molecules, such as molecules of a surfactant or a polymer, mostly of a nonionic type. These large molecules create a barrier, which prevents close contact of particles and their coalescence (the actual steric stabilization mechanism is more complex and involves osmotic pressure and entropy considerations). Steric stabilization is especially important for dispersions of metal NPs in organic media with low dielectric constant and for solvent-based conductive inks. An example of nonionic surfactant, which is used for stabilization of metal NPs, is a polyoxyethylene derivative, Triton X-100 (poly(oxyethylene)octyl phenyl ether) [43, 92]. However, the most effective steric stabilizers that are suitable for both aqueous and organic media are nonionic amphiphilic polymers, containing hydrophobic and hydrophilic components, and that are capable of interacting with both the metal NPs and the dispersion medium. Among them, poly(*N*-vinyl-2-pyrrolidone) (PVP) of various molecular weights is the most frequently used for stabilizing metal NPs, such as Ag and Cu, in various liquids and in nanoink formulations [12, 54, 67, 93–100]. This polymer strongly interacts with the metal NPs through the oxygen atom of

the carbonyl group [101]. Other nonionic polymers, which were reported to be stabilizers of metal NPs such as Ag and Cu, are poly(vinyl alcohol) (PVA) [98, 102–104] and poly(oxyethylene)-poly(oxypropylene) copolymer (Pluronic F127) [105].

In the case of charged polyelectrolytes, both electrostatic and steric mechanisms act simultaneously, resulting in “electrosteric” stabilization, which is especially effective in aqueous dispersions and inks [30]. Examples of electrosteric stabilizers are poly(acrylic acid) and its salts [66, 106–111] carboxymethyl cellulose sodium salt [112], poly(diallyldimethylammonium chloride) [113], poly(ethyleneimine) [114], commercial dispersants such as polynaphthalene sulfonate (Daxad 19 of Hampshire Chemical Corporation [115]), high-molecular-weight block copolymer with acidic affinic groups (Disperbyk-190 of BYK-Chemie [33]), anionic phosphated alkoxyated polymer Solsperse 40 000 of Lubrizol, and polycarboxylate ethers Sokalan HP80 of BASF [116].

For Ag and Au NPs, thiols ($R-SH$) are also widely used. They function through chemisorption on the surface of the particles [117]. The synthesis of Au NPs capped with water-insoluble alkanethiols is often performed in two-phase organic solvent (e.g., toluene)–water system [118–120]. Stabilization of Au NPs to be used for printed electronics by long-chain alkylamines was also reported [121, 122].

7.3.2.2 Stabilization Against Oxidation

In addition to aggregation stability, inks based on metal NPs should not undergo chemical transformations, which may affect the printing performance and conductivity of printed patterns.

Currently, most conductive nanoinks are based on silver NPs. Silver is a noble metal, which is resistant to oxidation and possesses the highest electrical conductivity among metals. However, large-scale production of printed electronic devices requires low-cost nanoinks, in which silver as a conductive functional material should be replaced by lower cost metals of high electrical conductivity such as copper and aluminum, having conductivities of about 95 and 55% of that of silver. The specific challenge while utilizing NPs of such metals is their oxidation at ambient conditions. For example, aluminum undergoes rapid (~ 100 ps) oxidation in air with the formation of very dense nonconductive Al_2O_3 layer, with a thickness of 2–6 nm [123, 124]. This obviously makes Al NPs inapplicable for the formulation of conductive nanoinks. Oxidation of Cu NPs is less rapid, compared to Al, especially in the presence of an excess of a reducing agent in the reaction mixture [108]. The same effect can be achieved by the addition of antioxidants to the dispersion of Cu NPs, for example, ascorbic acid or hydrazine, which are effective scavengers of free radicals and reactive oxygen molecules [125, 126]. To overcome the oxidation problem, the synthesis of Cu NPs is usually performed in organic solvents such as polyols [67, 68, 96, 100, 127–131], toluene [75], heptanes [132], octyl ether [133], octylamine [134], and often under inert atmosphere (Ar , N_2) [75, 132–134]. Regardless of the method of synthesis, to minimize the exposure of Cu NPs to oxygen, they should be coated by a dense protective layer of a capping agent [35]. Such layers can be formed by carboxylic

fatty acids (lauric, oleic) [75, 133–136], alkanethiols [135, 137, 138], surfactants such as bis(ethylhexyl)hydrogen phosphate (HDEHP) [132], CTAB [94, 127], and various polymers [35]. The advantage of using polymers is that the polymeric layer is dense enough to effectively slow down the oxygen penetration to the NP surface and, accordingly, to decrease the oxidation rate. The most widely used, both in organic solvents and in aqueous medium, is the amphiphilic PVP [67, 68, 77, 96, 100, 130, 131, 139]. The stability of Cu NPs can be further improved by using PVP and CTAB together as double capping agents [94].

Although these methods can considerably delay the oxidation of Cu NPs, they do not assure a long-term stability, which is required for commercial inkjet inks. A more effective approach toward obtaining stable metal NPs applicable for conductive ink formulations is the formation of a dense shell composed of a protective nonoxidizable material. For example, stable Cu NPs were obtained by the formation of a copper formate shell, by a reaction of a surface copper oxide with formic acid. This shell can be transformed into metallic copper during low-temperature (150 °C) annealing, resulting in highly conductive metallic films [140]. Cu NPs stable to oxidation were also produced by deposition of a thin (~3 nm) layer of graphene by the reducing flame technique, but the disadvantage of such core–shell NPs is the very low conductivity of the patterns printed with these NPs [141]. A more effective approach for obtaining protected NPs, which are suitable for the formulation of conductive nanoinks, is coating them with a protective shell composed of noble metals, that is, formation of bimetallic core–shell NPs (core@shell). Such nanoparticles can be obtained by transmetalation, which is a galvanic displacement reaction, when the surface of a preformed core functions (and is sacrificed) as a reducing agent for the second metal with higher reduction potential. By this process, the reduction of the second metal occurs only on the surface of the core metal, resulting in the formation of a metal shell on the surface of the core metal. The transmetalation method was used for the synthesis of Co@Au, Co@Pd, Co@Pt, Co@Cu [142], Ni@Au [143], and Cu@Ag [35, 108, 144–149] NPs. It has been demonstrated that Cu NPs, which are coated by a silver shell, possess high stability at ambient conditions in air, from 6 months [150] to 2 years [35, 108] while retaining their initial characteristics at elevated temperatures in the range of 150–250 °C [35, 108, 146, 148, 150].

7.4 Formulation of Conductive Metallic Nanoinks

As was noted in Section 7.2, inkjet ink for printed electronics contains a conductive nanomaterial, aqueous or organic liquid vehicle, and various additives that enable optimal printing performance and good quality of printed patterns [28, 29]. Since metallic nanoinks should provide high electrical conductivity of the printed patterns, it is essential that the content of the metal NPs is high. The higher the metal load in the ink, the higher the conductivity obtained from printing a given volume of droplets. Although the final conductivity of the printed patterns depends on several factors, including the number of printed

layers and postprinting process (see Section 7.5), high metal loading in ink formulation usually provides higher conductivity at one-layer printing, since the more concentrated the dispersion of metal NPs, the higher the number of contact points and percolation paths between NPs in the printed layers. To be of practical importance, conductive nanoink should contain metal NPs in the range of 20–80 wt% [151]. There are only a few reports on direct preparation of concentrated dispersions of metal NPs [2, 33, 106, 152–154], and usually the methods of formulating metallic nanoinks with high metal loading are based on a four-step procedure. The first step is the synthesis of metal NPs in the presence of stabilizing agent. Then, the synthesized NPs are separated by centrifugation or by precipitation with various organic solvents such as alcohols (methanol, ethanol, and isopropanol) or acetone. In the third step, the precipitated NPs are washed with a proper solvent to remove the excess of nonadsorbed materials such as dispersion stabilizers. The last stage is redispersing the obtained NPs in a proper liquid vehicle containing the required additives, usually by mechanical stirring, ultrasonication, and ball milling. This approach was successfully used for preparing Ag-based [33, 47, 66, 105, 155–160], Au-based [119, 161], and Cu-based [67, 75, 94, 96, 126, 131, 134, 136, 138, 139] nanoinks. Metal nanopowders prepared by the gas-phase [36], laser ablation, [162–164], and mechanochemical methods [165, 166] can also be used for conductive ink formulation. As to liquid vehicles, typical solvents are water [33, 51, 52, 75, 93, 105, 107–109, 112, 154, 167, 168], hydrocarbons such as toluene [118, 136, 153, 161, 169, 170], tetradecane [171], xylene [120], various oxygenated organic solvents such as 2-(2-butoxyethoxy)ethanol [67], tri(ethylene glycol) monomethyl ether [77], butoxy(ethylacetate) [172], terpineol [173, 174], and a mixture of solvents, for example, water and alcohol (ethanol, 2-ethoxyethanol, *n*-propanol, isopropanol, and cyclohexanol [130, 175–179]). Many metallic nanoinks contain various glycols as rheology modifiers and humectants [12, 65, 66, 94, 96, 116, 130, 139, 156, 175–180].

At present, there are a number of commercial metallic nanoinks on the market. For example, Ag inks with NP size in the range of 2–200 nm and metal loading in the range of 10–60 wt% are now being produced by companies such as NovaCentrix (USA), Sun Chemicals (USA), NanoMas (USA), Cabot Chemicals (USA), Applied Nanotech (USA), InkTec (Korea), Harima Chemicals (Japan), Advanced Nano Products (Korea), Samsung Electro-Mechanics (Korea), Cima NanoTech (USA), PV Nano Cell (Israel), Nano Dimension (Israel), DOWA Electronic Materials (Japan), UTDots Inc. (USA), and ULVAC GmbH (Germany).

Cu-based nanoinks containing 10–40 wt% metal (particles size 25–130 nm) are produced by NovaCentrix (USA), Intrinsiq Materials (USA), Applied Nanotech (USA), and Samsung Electro-Mechanics (Korea).

Gold nanoinks with metal loading of 10–50% and particle size of 2–10 nm are produced by ULVAC Technologies (USA), NanoMas (USA), and Harima Chemicals (Japan).

Activities in Ni nanoinks were reported by Applied Nanotech (USA, with particle size of 20–100 nm and metal content of 10–50%) and also by Intrinsiq Materials (USA).

Pd nanoinks are usually used for printing catalytic seeds, which are utilized in electroless processes for further deposition of Ni or Cu [10, 51, 52, 174].

7.5 Formation of 2D Conductive Structures: Printing and Sintering

Electrical resistivity is defined as follows:

$$\rho = R \cdot A / L \quad (7.1)$$

where ρ is the resistivity ($\Omega \text{ m}$, or $\mu\Omega \text{ cm}$), R is the measured resistance of a conductor, A is its cross-sectional area ($A = h \cdot W$, where h is film thickness and W is its width), and L is the conductor length [141]. For 2D films, the commonly used value in printed electronics is the sheet resistance, which is defined as follows:

$$R_{\text{sq}} \text{ (or } R) = \rho / h \quad (7.2)$$

Sheet resistance ($\Omega \square^{-1}$) can be directly measured by a four-point probe. It is convenient for the comparison of the resistivity of various 2D-printed patterns, without the need to measure the film thickness.

To obtain 2D-printed patterns with high electrical conductivity, which is close to that of bulk metal, a necessary condition is the formation of continuous direct contacts between the metal NPs within a printed layer. However, after printing and drying the ink, the presence of remaining insulating stabilizing agents (e.g., adsorbed polymeric or surfactant molecules) and other nonvolatile components of the ink in between the particles (such as wetting and rheological agents) prevents the formation of such contacts, thus resulting in low electrical conductivity. Therefore, the printing itself is the first step in obtaining the conductive structures, and a postprinting process in which the insulating materials are effectively removed is required. Such removal can be obtained by decomposition, desorption, or evaporation of the material to enable close contacts between the particles in the dried printed pattern, and eventually sintering. The conventional sintering method is based on heating the printed patterns to elevated temperatures, typically to 250–350 °C. However, this method is inapplicable for heat-sensitive substrates such as polymers (e.g., polyethylene terephthalate, PET, and polycarbonate, PC) and paper, which are widely used nowadays in flexible/plastics printed electronics and for large-area R2R printing [1, 2, 9, 151, 181]. Therefore, the current research and development of sintering methods focuses on avoiding destruction of heat-sensitive substrates. Later, we describe various methods for metal NPs sintering and the conductivities of the resulting printed structures.

Thermal sintering by heating the printed pattern to elevated temperatures is the most widely used method of sintering. High surface-to-volume ratio and enhanced self-diffusion of surface atoms make metal NPs much “softer” compared to large particles even at ambient temperature [182, 183]. This also results in a drastic decrease in melting point of metal NPs [182, 184] and their sintering (welding) at relatively low temperatures. The first step in such sintering is neck

formation between adjacent NPs in the printed layer, followed by formation of numerous percolation paths at temperatures much lower than the melting point of the bulk metal [1]. The temperature at which the printed layer undergoes sintering with formation of conductive metallic pattern depends on a number of factors, such as size of the particles in the ink, type of organic additives (e.g., polymeric stabilizers), and the number of printed layers [1, 2, 7, 151]. Usually, heating at 200–350 °C for 10–60 min is required to obtain sintered conductive 2D patterns printed on glass, silicon wafers, and polyimide with resistivity values only 2–15 times higher than the bulk resistivity of the respective metals: Ag [33, 47, 97, 185–188], Au [112], Cu [67, 75, 77, 94, 96, 138, 139, 189], Cu@Ag [108, 146], and Sn [65]. Sintering of patterns printed with Cu and Sn nanoinks is usually performed in vacuum, inert (N_2), or reductive (H_2) atmospheres. Figure 7.1 shows the changes in morphology of silver and copper 2D structures after heating at various temperatures. The critical changes in morphology with the formation of a continuous interconnection between Ag and Cu NPs are clearly seen at 260 and 300 °C, respectively. At 320 and 350 °C, the layers are well sintered with conductivities of about 50% and 10% of bulk metal, respectively [33, 139]. However, there are several reports on metal inks with lower sintering temperatures. For example, gold nanoinks stabilized with alkanethiols with 4–6 carbons were sintered at <150 °C on polyester films with resulting conductivity of 70% of bulk gold [118]. Conductive inkjet patterns printed on paper with silver ink containing polyacrylate as a stabilizing agent and sintered at 150 °C had resistivity only 3–5 times higher than that of bulk silver [167, 180]. Ink formulation containing low concentrations of weakly adsorbing stabilizers, such as poly(ethylene oxide) and poly(vinyl alcohol), enables obtaining conductive silver lines with 5% of bulk silver conductivity after sintering at temperature as low as 80 °C for 60 min [179].

Photonic sintering has recently been introduced as a promising alternative to thermal sintering of 2D printed structures [8, 9, 190–196]. It is based on selective

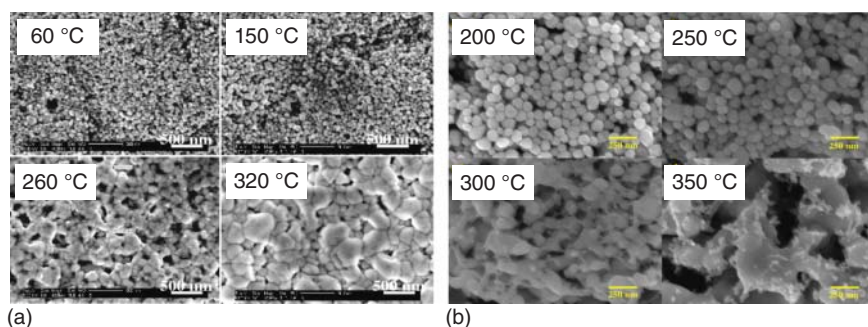


Figure 7.1 SEM images of 2D conductive structures as a function of sintering temperature. (a) Structures obtained by printing of aqueous silver nanoink (10% Ag, Disperbyk 190 as a dispersing agent) on a glass substrate and sintered in air atmosphere for 10 min. (Kamyshny *et al.* (2005) [33]. Reproduced with permission of Wiley.) (b) Structures obtained by printing copper nanoink (20% Cu in mixed solvent of ethylene glycol and 2-methoxyethanol, PVP as a stabilizing agent) on a glass substrate and sintered in vacuum for 1 h. (Park *et al.* (2007) [139]. Reproduced with permission of Elsevier.)

absorption of light, which results in localized heating of printed metallic patterns by using irradiation, which does not affect the substrate, a characteristic that is especially important for heat-sensitive plastic and paper substrates [8, 9]. Photonic sintering starts at the surface layer of printed NPs, and heat transfer from the surface leads to sintering the underlying NPs. Photonic sintering can be classified according to the range of excitation wavelengths: ultraviolet (UV), visible (intense photonic flash), and infrared (IR). Photonic sintering can also be performed by laser irradiation with single wavelength [9].

Photonic flash sintering using intense light pulse may be considered the most effective alternative method for conventional sintering, for obtaining highly conductive printed patterns on plastic substrates. This method is especially effective for R2R processing [8]. The most commonly used light source is Xe lamp, which emits radiation in a broad range of 200–1200 nm [9]. Since high-intensity UV light can damage plastic substrates, UV filters are often used. Flash sintering can also be optimized by controlling flashing frequency, intensity of pulse, and pulse duration [1, 9, 190, 197]. In the last years, flash sintering was successfully utilized for the sintering of 2D structures formed by Ag, Cu, Au, and Ni nanoinks deposited on glass [194], paper [136, 198], and various plastic substrates, such as polyimide (PI) [136, 195, 197, 199–204], PET [136, 205–207], polyethylene naphthalate (PEN) [8, 208], PC [197], polyethylene, and polypropylene [199]. With this technique, sintered silver, copper, and nickel 2D structures with resistivities in the range of 2–10 of bulk metals were obtained [136, 190, 191, 197, 199–201, 204, 207–209], while the morphology of the sintered layer was very similar to that obtained by thermal sintering (Figure 7.2). It should be noted that in contrast to thermal sintering, light flash sintering of Cu nanoinks can be performed in air because of the very fast kinetics of the process. In most cases, flash sintering results in reduction of the surface oxide layer [194, 199, 200, 202, 203]. As to the mechanism of such effects, the reduction of copper oxide in the case of PVP as

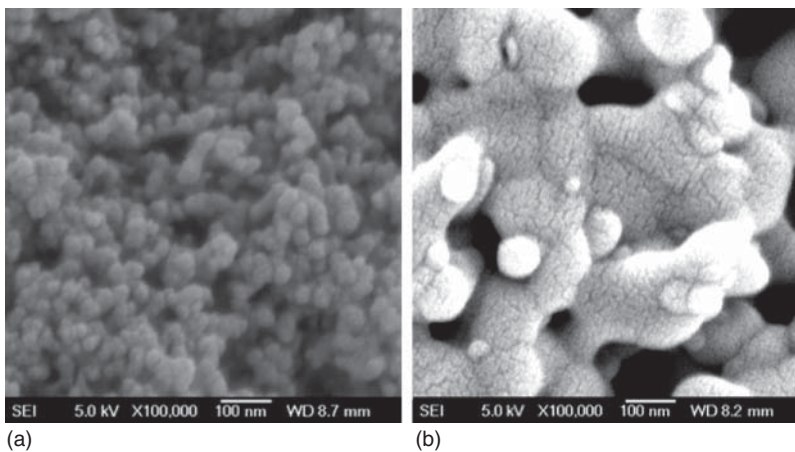


Figure 7.2 SEM images of 2D metallic structure obtained by inkjet printing of Cu nanoink on PI after drying (a) and following intense pulse irradiation (b). (Ryu *et al.* (2011) [200]. Reproduced with permission of Springer.)

a stabilizing agent may be attributed to intermediates that are formed under UV irradiation or to hydroxyl end groups, which are formed due to involvement of water and hydrogen peroxide in the polymerization process [200, 202].

The advantage of *laser sintering* is in using a focused laser beam with a tuned wavelength. Sintering of metal nanoinks can be performed by continuous wave (cw) Ar ion, cw or pulsed Nd:YAG, and diode solid-state lasers [9]. Since lasers can generate temperature up to 500 °C, laser sintering is mainly used for heat-stable substrates (glass, silicon, and PI) [169]. A cw laser heats the material more evenly, but pulse laser has a greater optical depth and smaller heat zone. Tuning the power output, wavelength, writing velocity, irradiation duration for cw lasers, or number of irradiation cycles for pulsed laser enables a decrease in temperature to 135–230 °C during sintering. For example, sintering of Ag nanoink printed on glass and PI substrates with the use of cw and pulse lasers resulted in resistivity values only 2.0–3.5 times higher than that of bulk silver [192, 197, 210]. Sintering of gold nanoink printed on glass substrates with cw Ar gas laser leads to a resistivity of 6 times higher than that of the bulk metal [193]. Effective sintering of Cu nanoinks printed on glass substrate with the use of visible cw laser [196] and on PI substrate with pulse UV laser [211] resulted in resistivities of 2–3 and 8 times higher than bulk copper resistivity, respectively. The advantage of laser sintering is that if it is performed fast enough, the oxidation of Cu NPs can be avoided even at ambient conditions [9]. The morphologies of laser-sintered patterns are similar to those formed after thermal sintering [192, 196, 197]. One more advantage of laser sintering is the possibility of high-resolution patterning by selective localization of the laser sintering of metal NPs, which is followed by the removal of ink that was not exposed to the radiation (unsintered NPs) [212].

IR sintering of printed nanoinks is performed by heating the printed patterns using irradiation in the range of 0.7–15 μm [9, 120, 191, 213, 214]. The advantage of such methods compared to conventional thermal sintering is the very short sintering time, in the range of 2–15 s [120, 213] to 3 min [214]. For example, silver and gold inkjet inks that were printed on paper were sintered within 15 s with resistivities of about 6 times higher compared to the bulk metals [120, 191].

Plasma sintering is usually performed by the exposure of printed patterns to low-pressure Ar plasma [7, 9, 181, 215, 216]. Plasma generation results in the formation of various excited species and UV irradiation, which causes decomposition of the organic components of the ink (such as stabilizing and wetting agents) and enables direct contact of metal NPs. Since the temperature during plasma sintering is usually less than 100 °C [217, 218], which is below the T_g of most plastic substrates, this method is especially useful for plastic electronics and can be utilized in R2R processes. The sintering process shows a clear evolution starting from the top layer into the bulk, and therefore obtaining high conductivity requires processing times of at least 30–60 min [9, 216]. Plasma sintering of Ag nanoinks printed on glass, PI, PC, and PET resulted in resistivities of 2.5–12 times of that for the bulk metal [197, 216, 218, 219]. To avoid the need for costly equipment for low-pressure plasma sintering, Ar plasma sintering at atmospheric pressure and room temperature was also developed. With this technique, 12% of bulk silver conductivity was achieved [220]. Printed Cu NPs stabilized by

PVP were sintered in a two-step process: treatment with atmospheric pressure O_2 plasma in order to decompose the PVP stabilizer at the first stage and with reductive H_2 plasma (in order to reduce the formed copper oxides) at the second stage. The obtained conductivity was up to 8% of bulk Cu [221].

Microwave sintering is based on fast (seconds to minutes) heating of printed metal layer by applying microwave radiation [222, 223]. Since metals have a very small penetration depth (1–2 μm for Ag, Au, and Cu at 2.54 GHz radiation), their sintering is successful only if the thickness of the printed layer is of the same order as the penetration depth. However, for metals such as silver, which is a good thermal conductor, the printed patterns will be heated uniformly by thermal conductance, enabling the microwave radiation to be applied to sintering patterns with a thickness exceeding the penetration depth. For example, treatment of Ag patterns on PI with an average height of 4.1 μm in constant-power (300 W) microwave reactor for 240 s resulted in conductivity 20 times lower than that of bulk silver [222]. Flash microwave sintering (1 s) of silver tracks printed on PEN foil, which was previously heated at 110 $^{\circ}C$ for 1–5 min, resulted in conductivity up to 34% of bulk silver [223]. Combining photonic and microwave flash treatments enabled obtaining 40% of bulk silver conductivity in less than 15 s [208]. Even better conductivity, 60% of bulk silver for 5-mm-long silver tracks printed on PEN foil was obtained in less than 10 min by combining low-pressure Ar plasma (150 W) presintering and microwave sintering (1 W power, 1 s flash) without damaging the polymeric substrate [217]. Figure 7.3 shows the morphology of such tracks, which is very similar to the morphologies obtained after thermal (Figure 7.1) and photonic sintering (Figure 7.2).

Electrical sintering is reached by applying a voltage to the printed pattern, and the DC electrical current causes local heating of the metallic layer. This method requires the printed pattern to be slightly conductive before sintering. The electrical sintering process takes place on a timescale of a few milliseconds to seconds [9, 181]. The conductivity of silver track on photo paper obtained with this method was reported to be more than 50% of bulk silver conductivity [224]. Silver nanoink printed on glass substrate forms a conductive pattern with resistivity

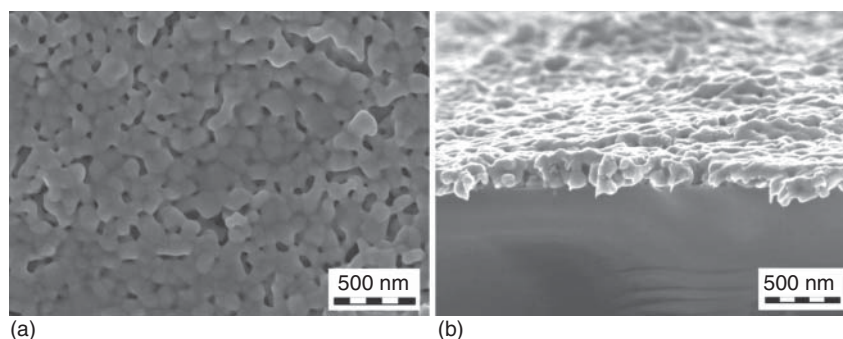


Figure 7.3 SEM images of Ag track printed on PEN foil after plasma presintering and microwave flash sintering resulting in a conductivity of 60% of that of bulk silver. a – top view, b – cross-sectional view. (Perelaer *et al.* (2012) [217]. Reproduced with permission of Wiley.)

3.3 times higher than that of bulk Ag [225]. In addition to DC electrical sintering, contactless AC electrical sintering was developed [226]. In this method, an AC field is applied by mobile electrodes, which are situated slightly above the sample [9, 226]. The electrical field overcomes the electrical gap, couples into the printed silver nanoink, and causes local sintering [9, 226].

Chemical sintering is based on desorption or decomposition of the protective layer on the surface of the NPs by chemical agents. For example, in the case of gold nanoinks stabilized by 1-butanethiol and deposited on glass, oxidation of the stabilizing agent by NO_2 resulted in the sintering of gold NPs, followed by a noticeable decrease in resistivity [227]. Another approach is dissolving the stabilizing molecules in a proper solvent. For example, treatment of printed Ag layer, which is composed of Ag NPs stabilized by dodecylamine and by methanol, leads to dissolving the stabilizing molecules and obtaining conductivity of about 2% of bulk Ag [228]. However, the majority of approaches do not involve a chemical reaction, but cause detachment (desorption) of the stabilizing layer [9]. Especially attractive are the recently developed methods of chemical sintering at room temperature (RT methods), which are applicable to heat- and intense light-sensitive substrates (paper, polymers, and textiles). These methods are based on coalescence of metal NPs, which is triggered by chemical agents [1, 2, 9, 109, 229].

It has been demonstrated that a drop of the polycation poly(diallyldimethylammonium chloride) (PDAC) placed on a printed layer of silver nanoink stabilized by polyacrylic acid (PAA) sodium salt caused immediate sintering of the NPs without any heating. The same effect also takes place when the silver nanoink is printed on a substrate that is precoated with PDAC solution. The obtained conductivities were found to be about 20% of that for bulk silver [229]. A similar sintering performance was observed for Cu@Ag NPs (20–50 nm) printed on photo paper [230]. As follows from the dependence of zeta potential on the concentration of PDAC, it acts as an effective coagulant for NPs stabilized by polyanionic PAA near the point of zero charge [229].

Another concept for RT sintering is based on the removal of a stabilizing agent by chemical agents, followed by spontaneous coalescence of metal NPs in printed layer. For example, contacting silver patterns printed on plastic substrates, with a NaCl solution followed by heating to 95 °C [231], immersing them in boiling saturated NaCl solution [232], or dipping in the same solution followed by ultrasonication [233] led to the detachment of the stabilizing polymers and consequently to a noticeable decrease in resistivity. High conductivity, about 30% of bulk silver, was achieved by sequential printing of silver nanoparticles ink and a “sintering” ink, which was composed of NaCl or MgCl_2 solutions, as shown schematically in Figure 7.4 [234]. Removal of the polymeric stabilizer in order to obtain high conductivity can also be accomplished by the exposure of printed patterns to HCl vapor [235].

The further development of this concept was “built-in” sintering approach for conductive nanoinks. This approach is based on triggering the coalescence of NPs in the printed layer during the drying stage. For example, Ag NPs that are stabilized by PAA undergo self-sintering spontaneously, due to the presence of a destabilizing agent, NaCl in the ink. Prior to printing, the concentration of NaCl

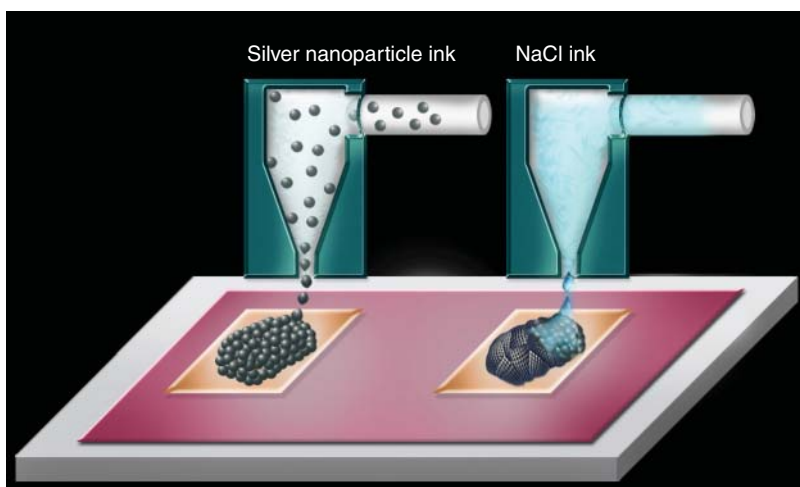


Figure 7.4 Scheme of the double printing process. First, a pattern of Ag nanoink is printed on the substrate followed by printing a salt solution on top of the silver pattern. (Layani *et al.* (2012) [234]. Reproduced with permission of Royal Society of Chemistry.)

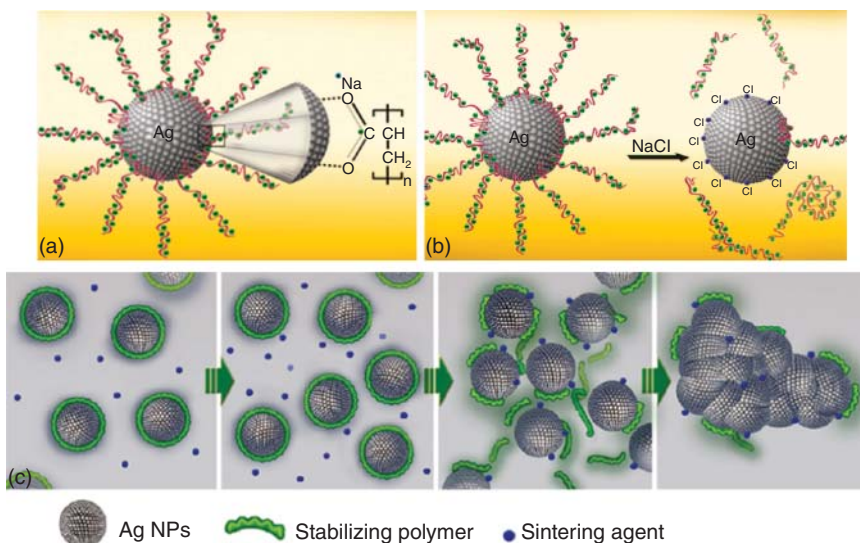


Figure 7.5 Schematic illustration of the stabilizer detachment followed by sintering caused by built-in sintering agent. (Grouchko *et al.* (2011) [109]. Reproduced with permission of American Chemical Society.)

is very low (up to 50 mM) and the ink is stable. After printing and during drying of the printed pattern, the concentration of the salt increases, and this causes a detachment of the polymeric stabilizer from the surface of NPs (Figure 7.5). The obtained conductivity of the printed silver patterns was reported to be as high as 40% of bulk silver [109].

7.6 3D Printing of Conductive Patterns: Formation and Sintering

Additive manufacturing and direct-write technologies offer the ability to construct 3D structures using a wide range of various materials. Such structures consisting of continuous solids can be fabricated through careful control of ink composition, its rheological behavior, and printing parameters [236, 237]. In this regard, 3D inkjet printing is a promising alternative to photolithography, etching, and filament-based direct writing [20, 238–243]. Two main types of conductive inkjet inks for printing 3D structures have been studied: metal NPs dispersed in volatile solvents and metal NPs dispersed in UV-curable liquids.

When using the first approach, metal pillars, wires, helices, zigzags, and micro-bridges were built on heated glass, silicon wafer, or polymer substrates, by additive printing of gold NPs dispersed in organic solvents [239, 241, 244]. Upon contact of the ink droplets with the heated substrate, the solvent immediately evaporates, thus increasing significantly the metal load and the ink viscosity and enabling fixation of each drop (with obvious shrinkage in droplet volume). Thermal sintering (150 °C) of formed 3D structures (bridge-shaped interconnectors) yielded electrical resistivity only 1.5 times higher compared to the bulk gold [244]. Conductive vertical pillars with a height of more than 60 μm and an aspect ratio of 50 and bridges were printed using Ag and Cu nanoinks by electrohydrodynamic inkjet printer on PI substrate. The resistivity of Ag bridges was found to be ~ 19 times of bulk silver [243]. 3D metal/insulator/metal crossovers were formed by sequential inkjet printing of first conductive Ag track, second UV/thermal cross-linkable insulator pad, and then second Ag track orthogonal to the first one on a glass slide. The resistivity of the Ag tracks was 26 times of that for bulk Ag [238].

UV-curable inks contain monomers or oligomers (such as acrylate derivatives) and photoinitiators capable of rapid polymerization upon irradiation with UV light, thus enabling immediate fixation of each printed droplet or layer and formation of a 3D structure by layer-by-layer printing on the same spot [28, 237]. Combining UV-curable composition with conductive NPs enables fabrication of conductive 3D patterns [240, 245]. For example, resistors were printed by using UV-curable inks based on a poly(ethylene glycol) diacrylate (PEGDA) matrix and a dispersion of aqueous silver NPs (10–50 wt%) [245]. For resistors, the presence of a large amount of insulating material, such as the polymerized monomers, is not very crucial. However, in order to obtain high conductivity, these materials present a major obstacle. To overcome this issue and to enable suitable percolation paths of the metallic NPs in printed 3D structure, a new, two-phase ink was reported, in which one phase brings the conductivity and the other phase brings the 3D structuring. This ink is composed of oil-in-water-type emulsion, in which the oil phase is composed of polymerizable acrylate monomers and initiators, and the water phase contains a dispersion of silver NPs. The ink was successfully applied for layer-by-layer inkjet printing of 3D conductors, and the conductivity achieved after RT chemical sintering by contact with NaCl solution was

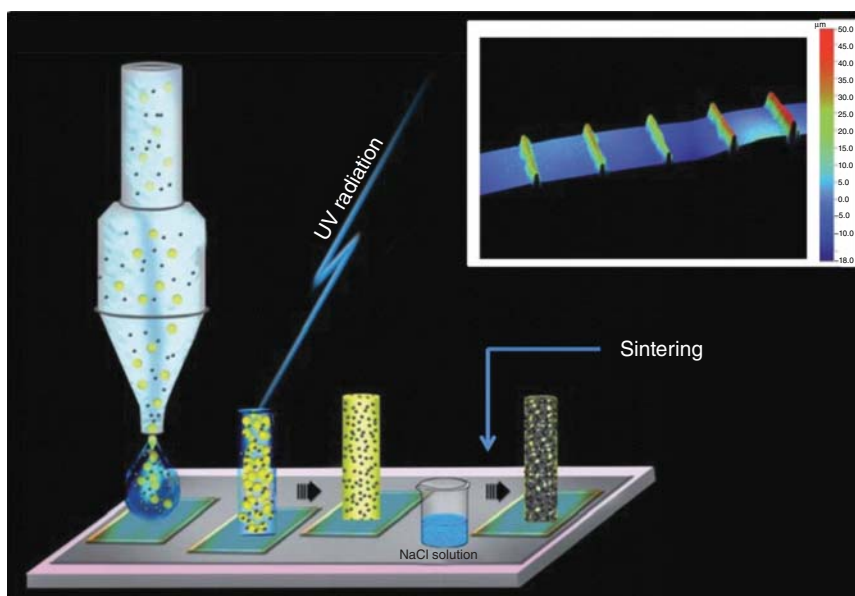


Figure 7.6 Printing of a conductive 3D structure with the use of ink composed of an UV-curable emulsion and a dispersion of silver NPs. Inset is a 3D profile of a 200 μm width lines composed of 1, 3, 6, 10, and 20 printed layers. (Layani *et al.* (2013) [240]. Reproduced with permission of Royal Society of Chemistry.)

about 3% of that for bulk Ag [240]. A scheme of the printing process is shown in Figure 7.6.

Recently, one more approach to fabrication of conductive 3D structures was reported [246]. A polymeric 3D object was formed with the use of UV-polymerizable oil-in-water emulsion by digital laser processing (DLP) method, which is based on selective polymerization of individual pixels within a thin layer. After polymerization to form the 3D object, the aqueous phase was evaporated, thus yielding a porous 3D object. In the next step, this object was immersed in the dispersion of Ag NPs and, by applying vacuum, the dispersion penetrated into the pores. After insertion of the NPs, the 3D object was exposed to HCl vapor, which led to chemical sintering as described earlier, and a conductive 3D structure was obtained.

7.7 Applications of Metallic Inkjet Nanoinks in Printed Electronics

In this section, we discuss several important applications of metallic nanoinks in printed electronics. This will include recent advances in fabrication of TCEs, which are nowadays essential for various optoelectronic devices, and inkjet-printed electronic devices, such as OSCs, RFID tags, TFTs, and light-emitting devices.

7.7.1 RFID Tags

RFID tag is a device that provides storing and remote reading of data from items equipped with such tags. The main elements of RFID tag are a microchip and an antenna, which provide power to the tag and communication with a reading device [6]. The antenna is typically fabricated by stamping/etching, silk screening, or lithographic techniques [2]. Fabrication of antennas on flexible substrates by inkjet printing of conductive inks is a promising approach to the production of low-cost RFID tags. Since the antenna should be of low resistivity (the read distance depends on the antenna conductivity), metal nanoinks are preferable. Appropriate processes for antenna fabrication by printing of silver nanoinks on PET [12, 218, 247], PEN [223], PI [247, 248], and paper [167]; copper nanoink on PET [12] and PI [249]; and Cu@Ag nanoink on paper [108, 230] were reported. Figure 7.7 presents RFID antenna printed on Epson photo paper with the use of Cu@Ag nanoinks [108].

7.7.2 Thin-Film Transistors

TFT is a special type of field-effect transistor made by deposition of thin films of a semiconductor layer as well as the dielectric layer and metallic contacts on a supporting nonconducting substrate. Metal NPs are also used to produce conductive features on both inorganic and organic TFTs. For example, gate and source/drain electrodes were inkjet-printed on TFTs with the use of Ag [25, 250–259], Au [260, 261], Cu [129, 262, 263], and mixed Ag–Cu [172] nanoinks.

7.7.3 Electroluminescent Devices and Light-Emitting Diodes

Electroluminescent (EL) devices are composed of a semiconductor layer placed between two electrodes and emit light in response to electric current. The conductive electrodes on these devices can be inkjet-printed by using various conductive nanomaterials including metal NPs, CNTs, and graphene [1]. Figure 7.8 shows flexible four-layer (PET:ITO:ZnS:BaTiO₃) EL device with patterned top Ag electrodes formed by inkjet printing of a silver nanoink onto the BaTiO₃ layer. Applying voltage (100 V) between the bottom ITO and the top Ag electrodes resulted in intense (90 cd m⁻²) emission of light [217, 229]. The sintering of the

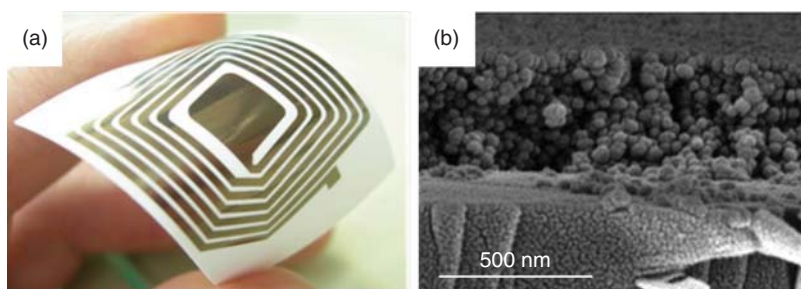


Figure 7.7 RFID antenna inkjet-printed on Epson photo paper with the use of Cu@Ag nanoink (a) and SEM image of the cross section of the printed pattern (b). (Grouchko *et al.* (2009) [108]. Reproduced with permission of Royal Society of Chemistry.)

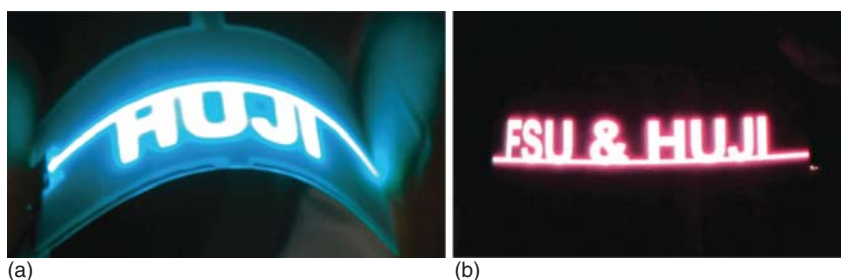


Figure 7.8 Working flexible four-layer electroluminescent devices (PET:ITO:ZnS:BaTiO₃) with patterned top Ag electrodes printed onto BaTiO₃ layer. (a) Ag pattern was sintered at RT by contact with a polycation, PDAC. Magdassi *et al.* (2010) [229]. Reproduced with permission. Copyright 2010, American Chemical Society. (b) Ag pattern was sintered by exposure to low-pressure Ar plasma. (Perelaer *et al.* (2012) [217]. Reproduced with permission of Wiley.)

printed patterns was performed by contact with a polycation (PDAC) at room temperature [229] or by exposure to low-pressure Ar plasma [217].

The conductive electrodes were also formed on GaN-based microstructured light-emitting diode (LED) [264] and on 3D extrusion-printed semiconductive quantum dot (CdSe/ZnS) LED [265] by using silver nanoinks.

7.7.4 Transparent Conductive Electrodes

At present, the dominating material for the fabrication of TCEs is indium tin oxide (ITO). However, ITO coatings have several drawbacks, such as high cost, complicated manufacturing process, and brittleness, the last one imposing severe limitation on its utilization in flexible electronics [1, 26]. Therefore, much effort is being made nowadays to find alternatives for ITO, which are based on nano-materials.

A common approach to fabricate metallic TCEs is by forming ultrathin (~ 10 nm) films deposited by DC sputtering or by patterning grids by using imprinting lithography [266, 267]. In one approach, to obtain transparent conductive coatings, 2D array and 2D network of overlapping metallic rings were formed based on “coffee-ring effect” by inkjet printing of drops of Ag nanoink on PET followed by RT sintering with HCl vapor (Figure 7.9). The

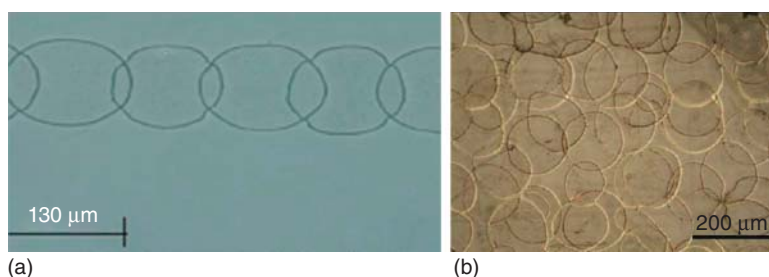


Figure 7.9 Light microscope images of a 2D array (a) and a 2D network (b) of conductive Ag rings inkjet printed on PET. (Layani *et al.* (2009) [268]. Reproduced with permission of American Chemical Society.)

resulting array of silver rings with rims $<10\text{ }\mu\text{m}$ in width and $<300\text{ nm}$ in height had high transparency and sheet resistance of $4\text{ }\Omega\text{ }\square^{-1}$, and could be used as the transparent electrode in an EL device [268].

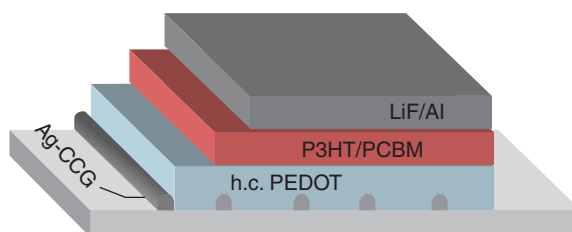
The coffee ring effect was also utilized for inkjet printing of parallel lines (“coffee lines”) composed of Ag NPs and having a width of $5\text{--}10\text{ }\mu\text{m}$, height of $0.6\text{--}0.8\text{ }\mu\text{m}$, and a distance of $60\text{--}80\text{ }\mu\text{m}$ between two adjacent lines. The resistivity of such lines printed on glass and sintered at $160\text{--}200\text{ }^{\circ}\text{C}$ was up to 36 times of that for bulk silver [93]. The 2D pattern of intersecting lines printed on PET and sintered at RT by HCl vapors was found to be $30\text{ }\Omega\text{ }\square^{-1}$ [111]. The transparency of the printed patterns was 91.2% and 93.6%, respectively. Grids formed by electrohydrodynamic jet printing of Ag nanoinks on glass substrate (distance between adjacent lines is $150\text{ }\mu\text{m}$) had a sheet resistance of $4.87\text{ }\Omega\text{ }\square^{-1}$ and transmittance of 81.75% after annealing at $200\text{ }^{\circ}\text{C}$ [269]. Coating of printed Ag grids (line width $7.5\text{ }\mu\text{m}$, line height $14\text{ }\mu\text{m}$, distance between lines $300\text{ }\mu\text{m}$) with ITO layer by brush painting followed by sintering at $200\text{ }^{\circ}\text{C}$ resulted in a very low sheet resistance of $1.4\text{ }\Omega\text{ }\square^{-1}$ and transmittance of 83.72% [270]. To form flexible TCEs, Ag grids that were inkjet-printed on PET substrate were also combined with graphene films synthesized using a chemical vapor deposition method [271]. The obtained TCEs had a sheet resistance of $11.5\text{--}12.8\text{ }\Omega\text{ }\square^{-1}$ and transmittance of 70.8–74.5%. Transparent grids were also prepared by inkjet printing of Cu nanoink on glass substrate followed by annealing at $500\text{ }^{\circ}\text{C}$ in a mixture of N_2 and H_2 [272]. The optical transmittance of obtained Cu grids was high, 89.66%, but the resistivity was also high, about 130 times of that for bulk copper.

Metal NWs are also promising material for the fabrication of flexible TCEs. An important feature of NW-based TCEs is their mechanical stability under repeated bending and retention of conductivity [1, 26, 273]. It should be noted that the use of NWs for making transparent electrodes by nonprinting methods is out of the scope of this chapter. Among the methods of fabrication of NW-based TCEs, inkjet printing is the most challenging because of high aspect ratio of metal NWs (diameters of $40\text{--}100\text{ nm}$ and length up to $30\text{ }\mu\text{m}$ [274–276]) that makes it difficult to print their dispersion without blocking the jetting nozzles. Only very few reports on the fabrication of TCEs by inkjet printing of metal NWs were published during the last years [277, 278]. For example, Ag NWs were inkjet-printed on the PEDOT:PSS:MoO₃ layer on glass substrate, and the network formed after the deposition of nine layers was characterized by a sheet resistance of $26.4\text{ }\Omega\text{ }\square^{-1}$ and transmittance of 83% [277]. Printing of Ag NWs on PET substrate followed by heating at $110\text{ }^{\circ}\text{C}$ resulted in TCEs with a sheet resistance of $8\text{ }\Omega\text{ }\square^{-1}$ [278]. It has been demonstrated in these reports that optimization of printing parameters and ink composition enables preventing the nozzle clogging and obtaining uniform 2D networks. One of important practical applications of grid-based TCEs is collecting electrodes for OSCs.

7.7.5 Organic Solar Cells

Solar cells are photovoltaic devices that convert solar radiation to electrical current. In fact, SCs are large-area semiconductor diodes based mainly on crystalline silicon (more than 85% of the world market) [2]. In the last years, OSCs attracted

Figure 7.10 Schematic presentation of typical OSC. (Galagan *et al.* (2013) [283]. Reproduced with permission of Elsevier.)



a great scientific attention. The advantages of OSCs are flexibility (if plastic flexible films are used as substrates), light weight, and low fabrication costs [279]. The electrical current in OSCs is collected by a metallic electrode – current collecting grid (CCG), which does not cover the entire face of the front side of the OSCs to allow maximum visible light to pass through the cell. The conventional method of electrodes production is screen printing of silver pastes. In recent years, silver NPs and NWs have been also used for the fabrication of conductive electrodes of OSCs by direct inkjet printing, which is also applicable for large-scale fabrication of flexible SCs by R2R approach [280–282]. Figure 7.10 presents a scheme of a typical OSC with inkjet-printed Ag-CCG coated by inkjet-printed layer of highly conductive PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate). On the top of this layer, a photoactive blend P3HT/PCBM (poly(3-hexylthiophene)/[6,6]-phenyl- C_{61} -butyric acid methyl ester) was spin coated and then cathode (upper layer) was deposited by thermal evaporation of LiF and Al [283].

As substrates for printing the Ag-CCGs with silver nanoinks, glass [279, 283–293], PET, [281, 282], and PEN [283] were used. Recently, OSC electrodes were formed on PET by combining inkjet-printed Ag-CCG with a graphene film, which was synthesized by chemical vapor deposition [271] and by inkjet printing of Ag NWs on the surface of PEDOT:PSS:MoO₃ layer on a glass substrate [277].

7.8 Outlook

Nowadays, printed electronics shows a significant growth on a number of levels, and some applications move from lab studies to prototypes, pilot production, and industrial manufacturing. All printed electronic devices contain an electrical conductor, and therefore the fast growth in this field requires the development of highly efficient and robust conductive inks and related technologies. This will require developing new materials, optimization of ink formulations, optimal tailoring of ink–substrate interaction, and improvement of manufacturing technologies and equipment. We expect that this would lead to optimal performance of the whole printing system in order to fabricate highly effective electronic devices such as TCEs, SCs, LEDs, RFID tags, TFTs, displays, and touch screens by additive manufacturing technologies. For example, TCEs still require improving optical properties, adhesion and bending stability at high electrical conductivity, combined with suitable patterning technologies by printing.

Since cost versus performance is a crucial issue, moving from the commonly used silver inks to low-cost inks, which are composed of conductive materials

such as copper, aluminum, and nickel, is now of primary interest. Therefore, during the last years, many researchers focused on formation of air-stable Cu-based nanoinks.

Additional major challenge in the field of flexible printed electronics (plastic substrates and paper) is developing highly efficient postprinting sintering processes, which is crucial for obtaining plastic devices. Such sintering processes should be performed at low temperatures, usually not higher than 150 °C to prevent damage of heat-sensitive substrates. Although a number of various not-damaging sintering approaches were developed during the last years, implementation in large scale still requires improvement of existing technologies and development of new ones to obtain highly conductive printed patterns.

Finally, an important perspective in the application of conductive nanomaterials is 3D printing of conductive patterns to address the needs of future additive manufacturing technologies. Nowadays, this field is at its early stages of research and development, and the search for new nanomaterials as well as suitable 3D fabrication tools based on wet deposition is a stimulating challenge for materials scientists.

References

- 1 Kamyshny, A. and Magdassi, S. (2014) Conductive nanomaterials for printed electronics. *Small*, **10** (17), 3515–3535.
- 2 Kamyshny, A., Steinke, J., and Magdassi, S. (2011) Metal-based inkjet inks for printed electronics. *Open Appl. Phys. J.*, **4**, 19–36.
- 3 Singh, M., Haverinen, H.M., Dhagat, P., and Jabbour, G.E. (2010) Inkjet printing – process and its applications. *Adv. Mater.*, **22** (6), 673–685.
- 4 Perelaer, J. and Schubert, U.S. (2012) Inkjet printing of interconnects and contacts based on inorganic nanoparticles for printed electronic applications, in *Inkjet-Based Micromanufacturing* (eds J.P. Korvink, P.J. Smith, and D.-Y. Shin), Wiley-VCH, Weinheim, Germany, pp. 347–364.
- 5 Cummins, G. and Desmulliez, M.P.Y. (2012) Inkjet printing of conductive materials: A review. *Circuit World*, **38** (4), 193–213.
- 6 Subramanian, V. (2012) Antennas for radio frequency identification tags, in *Inkjet-Based Micromanufacturing* (eds J.P. Korvink, P.J. Smith, and D.-Y. Shin), Wiley-VCH, Weinheim, Germany, pp. 313–329.
- 7 Perelaer, J., Smith, P.J., Mager, D., Soltman, D., Volkman, S.K., Subramanian, V., Korvink, J.G., and Schubert, U.S. (2010) Printed electronics: The challenges involved in printing devices, interconnects, and contacts based on inorganic materials. *J. Mater. Chem.*, **20** (39), 8446–8453.
- 8 Abbel, R., Teunissen, P., Rubingh, E., van Lammeren, T., Cauchois, R., Evaraars, M., Valetton, J., van de Geijn, S., and Groen, P. (2014) Industrial-scale inkjet printed electronics manufacturing – production up-scaling from concept tools to a roll-to-roll pilot line. *Transl. Mater. Res.*, **1** (1), 015002(1–13).

- 9 Wünscher, S., Abbel, R., Perelaer, J., and Schubert, U.S. (2014) Progress of alternative sintering approaches of inkjet printed metal inks and their application for manufacturing of flexible electronic devices. *J. Mater. Chem. C*, **2** (48), 10232–10261.
- 10 Gysling, H.J. (2014) Nanoinks in inkjet metallization – evolution of simple additive-type metal patterning. *Curr. Opin. Colloid Interface Sci.*, **19** (2), 155–162.
- 11 Tekin, E., Smith, P.J., and Schubert, U.S. (2008) Inkjet printing as a deposition and patterning tool for polymers and inorganic particles. *Soft Matter*, **4** (4), 703–713.
- 12 Dang, M.C., Dang, T.M.D., and Fribourg-Blanc, E. (2013) Inkjet printing technology and conductive inks synthesis for microfabrication techniques. *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **4** (1), 015009(1–7).
- 13 Printed electronics market. Available from: <http://www.marketsandmarkets.com/Market-Reports/printed-electronics-market-197.html>.
- 14 Wang, S., Liu, N., Yang, C., Liu, W., Su, J., Li, L., Yang, C., and Gao, Y. (2015) Fully screen printed highly conductive electrodes on various flexible substrates for asymmetric supercapacitors. *RSC Adv.*, **5** (104), 85799–85805.
- 15 Venkata, A.K., Venkata, K.R., Karthik, P.S., and Surya, P.S. (2015) Copper conductive inks: Synthesis and its utilization in flexible electronics. *RSC Adv.*, **5** (79), 63985–64030.
- 16 Yin, W., Lee, D.-H., Choi, J., Park, C., and Cho, S.M. (2008) Screen printing of silver nanoparticle suspension for metal interconnects. *Korean J. Chem. Eng.*, **25** (6), 1358–1361.
- 17 Lim, S.C., Kim, S.H., Yang, Y.S., Lee, M.Y., Nam, S.Y., and Ko, J.B. (2009) Organic thin-film transistor using high-resolution screen-printed electrodes. *Jpn. J. Appl. Phys.*, **48** (8R), 081503(1–3).
- 18 Vinod, P.N. (2013) The electrical and microstructural properties of electroplated screen-printed Ag metal contacts in crystalline silicon solar cells. *RSC Adv.*, **3** (33), 14106–14113.
- 19 Hyun, W.J., Lim, S., Ahn, B.Y., Lewis, J.A., Frisbie, C.D., and Francis, L.F. (2015) Screen printing of highly loaded silver inks on plastic substrates using silicon stencils. *ACS Appl. Mater. Interfaces*, **7** (23), 12619–12624.
- 20 Ahn, B.Y., Duoss, E.B., Motala, M.J., Guo, X., Park, S.I., Xiong, Y., Yoon, J., Nuzzo, R.G., Rogers, J.A., and Lewis, J.A. (2009) Omnidirectional printing of flexible, stretchable, and spanning silver microelectrodes. *Science*, **323** (5921), 1590–1593.
- 21 Ahn, B.Y., Lorang, D.J., and Lewis, J.A. (2011) Transparent conductive grids via direct writing of silver nanoparticle inks. *Nanoscale*, **3** (7), 2700–2702.
- 22 Lewis, J.A. and Ahn, B.Y. (2015) Three-dimensional printed electronics. *Nature*, **518** (7537), 42–43.
- 23 Teichler, A., Perelaer, J., and Schubert, U.S. (2013) Inkjet printing of organic electronics – comparison of deposition techniques and state-of-the-art developments. *J. Mater. Chem. C*, **1** (10), 1910–1925.
- 24 Pabst, O., Perelaer, J., Beckert, E., Schubert, U.S., Eberhardt, R., and Tünnermann, A. (2013) All inkjet-printed piezoelectric polymer actuators:

- Characterization and applications for micropumps in lab-on-a-chip system. *Org. Electron.*, **14** (12), 3423–3429.
- 25 Fukuda, K., Sekine, T., Kumaki, D., and Tokito, S. (2013) Profile control of inkjet printed silver electrodes and their application to organic transistors. *ACS Appl. Mater. Interfaces*, **5** (9), 3916–3920.
 - 26 Layani, M., Kamyshny, A., and Magdassi, S. (2014) Transparent conductors composed of nanomaterials. *Nanoscale*, **6** (11), 5581–5591.
 - 27 Layani, M., Darmawan, P., Foo, W., Liu, L., Kamyshny, A., Mandler, D., Magdassi, S., and Lee, P.S. (2014) Nanostructures electrochromic films by inkjet printing on large area and flexible transparent silver electrodes. *Nanoscale*, **6** (9), 4572–4576.
 - 28 Kamyshny, A. and Magdassi, S. (2012) Inkjet ink formulations, in *Inkjet-Based Micromanufacturing* (eds J.P. Korvink, P.J. Smith, and D.-Y. Shin), Wiley-VCH, Weinheim, Germany, pp. 173–189.
 - 29 Kamyshny, A. and Magdassi, S. (2013) Inkjet printing, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-VCH, Weinheim, Germany, pp. 1–21.
 - 30 Kamyshny, A. and Magdassi, S. (2010) Aqueous dispersions of metallic nanoparticles. Preparation, stabilization, and application, in *Nanoscience: Colloidal and Interfacial Aspects* (ed. V. Starov), CRC Press, Boca Raton, London, New York, pp. 747–778.
 - 31 Farraj, Y., Grouchko, M., and Magdassi, S. (2015) Self-reduction of a copper complex MOD ink for inkjet printing conductive patterns on plastics. *Chem. Commun.*, **51**, 1587–1590.
 - 32 Rae, A. and Hammer-Fritzing, D. (2006) Creating metal and nonmetal nanosystems using conductive jettable inks. *Solid State Technol.*, **49** (4), 53–55.
 - 33 Kamyshny, A., Ben-Moshe, M., Aviezer, S., and Magdassi, S. (2005) Ink-jet printing of metallic nanoparticles and microemulsions. *Macromol. Rapid Commun.*, **26** (4), 281–288.
 - 34 Magdassi, S. (2010) Ink requirements and formulations guidelines, in *Chemistry of Inkjet Inks* (ed. S. Magdassi), World Scientific, New Jersey, London, Singapore, pp. 19–41.
 - 35 Magdassi, S., Grouchko, M., and Kamyshny, A. (2010) Copper nanoparticles for printed electronics: Routes towards achieving oxidation stability. *Materials*, **3** (9), 4626–4638.
 - 36 Kimura, K. (2000) Formation in gas phases, in *Fine Particles: Synthesis, Characterization, and Mechanism of Growth* (eds M.J. Schick and A.T. Hubbard), Marcel Dekker, New York-Basel, pp. 513–550.
 - 37 Schmid, G. (2001) Metals, in *Nanoscale Materials in Chemistry* (ed. K.J. Klabunde), John Wiley & Sons, New York, pp. 15–59.
 - 38 Teranishi, T. (2012) Metallic colloids, in *Encyclopedia of Surface and Colloid Science* (ed. P. Somasundaram), Taylor & Francis, Boca Raton, pp. 3662–3674.
 - 39 Tretyakov, Y.D., Lukashin, A.V., and Eliseev, A.A. (2004) Synthesis of functional nanocomposites based on solid-phase nanoreactors. *Russ. Chem. Rev.*, **73** (9), 899–921.

- 40 Pitkethly, M.J. (2004) Nanomaterials – the driving force. *Mater. Today*, **7** (12), 20–29.
- 41 Kotov, Y.A. (2003) Electric explosion of wires as a method for preparation of nanopowders. *J. Nanopart. Res.*, **5** (5–6), 539–550.
- 42 Kim, W., Park, J.S., Suh, C.Y., Lee, J.C., Kim, J., and Oh, Y.J. (2007) A new method for the production of alloy nanoparticles by electrical wire explosion. *Mater. Trans.*, **48** (7), 1973–1974.
- 43 Sakamoto, M., Fujistuka, M., and Majima, T. (2009) Light as a construction tool of metal nanoparticles: Synthesis and mechanism. *J. Photochem. Photobiol., C*, **10** (1), 33–56.
- 44 Fiévet, F. (2000) Polyol process, in *Fine Particles: Synthesis, Characterization, and Mechanism of Growth* (eds M.J. Schick and A.T. Hubbard), Marcel Dekker, New York, Basel, pp. 460–496.
- 45 Toshima, N. (2000) Reactions in homogeneous solutions, in *Fine Particles: Synthesis, Characterization, and Mechanism of Growth* (eds M.J. Schick and A.T. Hubbard), Marcel Dekker, New York, Basel, pp. 430–459.
- 46 Dupont, J., Fonseca, G.S., Umpierre, A.P., Fichtner, P.F.P., and Teixeira, S.R. (2002) Transition-metal nanoparticles in imidazolium ionic liquids: Recyclable catalysts for biphasic hydrogenation reactions. *J. Am. Chem. Soc.*, **124** (16), 4228–4229.
- 47 Jung, I., Jo, Y.H., Kim, I., and Lee, H.M. (2012) A simple process for synthesis of Ag nanoparticles and sintering of conductive ink for use in printed electronics. *J. Electron. Mater.*, **41** (1), 115–121.
- 48 Philippot, K. and Chaudret, B. (2003) Organometallic approach to the synthesis and surface reactivity of noble metal nanoparticles. *C. R. Chim.*, **6** (8–10), 1019–1034.
- 49 Green, M. (2005) Organometallic based strategies for metal nanocrystal synthesis. *Chem. Commun.*, 3002–3011.
- 50 Butovsky, E., Perelshstein, I., Nissan, I., and Gedanken, A. (2013) Fabrication, characterization, and printing of conductive ink based on multi core-shell nanoparticles synthesized by RAPET. *Adv. Funct. Mater.*, **23** (46), 5794–5799.
- 51 Wang, M.-W., Liu, T.-Y., Pang, D.-C., Hung, J.-C., and Tseng, C.-C. (2014) Inkjet printing of a pH sensitive catalyst patterns of ITO glass for electroless copper. *Surf. Coat. Technol.*, **259** (B), 340–345.
- 52 Chen, W.-D., Lin, Y.-H., Chang, C.-P., Sung, Y., Liu, Y.-M., and Ger, M.-D. (2011) Fabrication of high-resolution conductive line via inkjet printing of nano-palladium catalyst onto PET substrate. *Surf. Coat. Technol.*, **205** (20), 4750–4756.
- 53 Liz-Marzán, L.N. (2004) Nanomaterials: Formation and color. *Mater. Today*, **7** (2), 26–31.
- 54 Sun, Y. and Xia, Y. (2003) Gold and silver nanoparticles: A class of chromophores with colors tunable in the range from 400 to 750 nm. *Analyst*, **128** (6), 686–691.
- 55 Goia, D.V. and Matijević, E. (1998) Preparation of monodispersed metal particles. *New J. Chem.*, **22** (11), 1203–1215.

- 56 Park, J., Privman, V., and Matijević, E. (2001) Model of formation of monodispersed colloid. *J. Phys. Chem. B*, **105** (47), 11630–11635.
- 57 Murphy, C.J., Sau, T.K., Gole, A.M., Orendorff, C.J., Gao, J., Gou, L., Hunyadi, C.E., and Li, T. (2005) Anisotropic metal nanoparticles: Synthesis, assembly, and optical applications. *J. Phys. Chem. B*, **109** (29), 13857–13870.
- 58 Goia, D.V. (2004) Preparation and formation mechanisms of uniform metallic particles in homogeneous solutions. *J. Mater. Chem.*, **14** (4), 451–458.
- 59 Antelman, M.S. (1982) *Chemical Electrode Potentials*, Plenum Press, New York, London.
- 60 Couto, G.G., Klein, J.J., Schreiner, W.H., Mosca, D.H., de Oliveira, A.J.A., and Zarbin, A.J.G. (2007) Nickel nanoparticles obtained by a modified polyol process: Synthesis, characterization, and magnetic properties. *J. Colloid Interface Sci.*, **311** (2), 461–468.
- 61 Bai, L., Yuan, F., and Tang, Q. (2008) Synthesis of nickel nanoparticles with uniform size via a modified hydrazine reduction route. *Mater. Lett.*, **62** (15), 2267–2270.
- 62 Eluri, R. and Paul, B. (2012) Synthesis of nickel nanoparticles by hydrazine reduction: Mechanistic study and continuous flow synthesis. *J. Nanopart. Res.*, **14** (4), 800(1–14).
- 63 Singh, K., Kate, K.H., Chilukuri, V.V.S., and Khanna, P.K. (2011) Glycerol mediated low temperature synthesis of nickel nanoparticles by solution reduction method. *J. Nanosci. Nanotechnol.*, **11** (6), 5131–5136.
- 64 Jiang, H., Moon, K., Dong, H., Hua, F., and Wong, C.P. (2006) Size-dependent melting properties of tin nanoparticles. *Chem. Phys. Lett.*, **429** (4–6), 492–496.
- 65 Jo, Y.H., Jung, I., Choi, C.S., Kim, I., and Lee, H.M. (2011) Synthesis and characterization of low temperature Sn nanoparticles for the fabrication of highly conductive ink. *Nanotechnology*, **22** (22), 225701(1–8).
- 66 Shen, W., Zhang, X., Huang, Q., Xu, Q., and Song, W. (2014) Preparation of solid silver nanoparticles for inkjet printed flexible electronics with high conductivity. *Nanoscale*, **6** (3), 1622–1628.
- 67 Lee, Y., Choi, J.R., Lee, K.J., Stott, N.E., and Kim, D. (2008) Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics. *Nanotechnology*, **19** (41), 415604(1–7).
- 68 Tang, X.F., Yang, Z.G., and Wang, W.J. (2010) A simple way of preparing high-concentration and high-purity nano copper colloid for conductive ink in inkjet printing technology. *Colloids Surf, A*, **360** (1–3), 99–104.
- 69 Bonet, F., Delmas, V., Grugeon, S., Herrera Urbina, R., Silvert, P.-Y., and Tekaiia-Elhsissen, K. (1999) Synthesis of monodisperse Au, Pt, Pd, Ru and Ir nanoparticles in ethylene glycol. *Nanostruct. Mater.*, **11** (8), 1277–1284.
- 70 Hei, H., He, H., Wang, R., Liu, X., and Zhang, G. (2012) Controlled synthesis and characterization of noble metal nanoparticles. *Soft Nanosci. Lett.*, **2** (3), 34–40.
- 71 Wiley, B., Sun, Y., Mayers, B., and Xia, Y. (2005) Shape-controlled synthesis of metal nanostructures: The case of silver. *Chem. Eur. J.*, **11** (2), 454–463.

- 72 Sun, Y. and Xia, Y. (2002) Large-scale synthesis of uniform silver nanowires through a soft, self-seeding, polyol process. *Adv. Mater.*, **14** (11), 833–837.
- 73 Tang, X. and Tsuji, M. (2010) Synthesis of silver nanowires in liquid phase, in *Nanowires Science and Technology* (ed. N. Lupu), InTech, Rijeka, Croatia, Shanghai, China, pp. 25–42.
- 74 Yin, Z., Lee, C., Cho, S., Yoo, J., Piao, Y., and Kim, Y.S. (2014) Facile synthesis of oxidation-resistance copper nanowires toward solution-processable, flexible, foldable, and free-standing electrodes. *Small*, **10** (24), 5047–5052.
- 75 Jeong, S., Song, H.C., Lee, W.W., Lee, S.S., Choi, Y., Son, W., Kim, E.D., Paik, C.H., Oh, S.H., and Ryu, B.H. (2011) Stable aqueous based Cu nanoparticle ink for printing well-defined highly conductive features on a plastic substrate. *Langmuir*, **27** (6), 3144–3149.
- 76 Starowicz, M., Stypuła, B., and Banaś, J. (2006) Electrochemical synthesis of silver nanoparticles. *Electrochem. Commun.*, **8** (2), 227–230.
- 77 Cheon, J., Lee, J., and Kim, J. (2012) Inkjet printing using copper nanoparticles synthesized by electrolysis. *Thin Solid Films*, **520** (7), 2639–2643.
- 78 Dhas, N.A., Raj, C.P., and Gedanken, A. (1998) Synthesis, characterization, and properties of metallic copper nanoparticles. *Chem. Mater.*, **10** (5), 1446–1452.
- 79 Yang, G.W. and Li, H. (2008) Sonochemical synthesis of highly monodispersed and size controllable Ag nanoparticles in ethanol solution. *Mater. Lett.*, **62** (14), 2189–2191.
- 80 Haas, I., Shanmugam, S., and Gedanken, A. (2006) Pulsed sonoelectrochemical synthesis of size-controlled copper nanoparticles stabilized by poly(*N*-vinylpyrrolidone). *J. Phys. Chem. B*, **110** (34), 16947–16952.
- 81 Kapoor, S. (1998) Preparation, characterization, and surface modification of silver particles. *Langmuir*, **14** (5), 1021–1025.
- 82 Henglein, A. and Giersig, M. (1999) Formation of colloidal silver nanoparticles: capping action of citrate. *J. Phys. Chem. B*, **103** (44), 9533–9539.
- 83 Kapoor, S. (1999) Effect of ligands on the redox reactions of silver metal clusters. *Langmuir*, **15** (13), 4365–4369.
- 84 Tadros, T. (2007) General principles of colloid stability and the role of surface sources, in *Colloid Stability: The Role of Surface Forces; Part I* (ed. T.F. Tadros), Wiley-VCH, Weinheim, pp. 1–22.
- 85 Zhang, Z. and Han, M. (2003) Template-directed grows from small clusters to uniform silver nanoparticles. *Chem. Phys. Lett.*, **374** (1–2), 91–94.
- 86 Wu, S.-H. and Chen, D.-H. (2004) Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions. *J. Colloid Interface Sci.*, **273** (1), 165–169.
- 87 Chen, L., Zhang, D., Chen, J., Zhou, H., and Wan, H. (2006) The use of CTAB to control the size of copper nanoparticles and the concentration of alkylthiols on their surfaces. *Mater. Sci. Eng., A*, **415** (1–2), 156–161.
- 88 Pal, T., Sau, T.K., and Jana, N.R. (1997) Reversible formation and dissolution of silver nanoparticles in aqueous surfactant media. *Langmuir*, **13** (6), 1481–1485.

- 89 Joshi, S.S., Patil, S.F., Iyer, V., and Mahumuni, S. (1998) Radiation induced synthesis and characterization of copper nanoparticles. *Nanostruct. Mater.*, **10** (7), 1135–1144.
- 90 Liz-Marzán, L.M. and Lado-Touriño, I. (1996) Reduction and Stabilization of Silver Nanoparticles in Ethanol by Nonionic Surfactants. *Langmuir*, **12** (15), 3585–3589.
- 91 Wang, W., Efrima, S., and Regev, O. (1998) Directing oleate stabilized nano-sized silver colloids into organic phases. *Langmuir*, **14** (3), 602–610.
- 92 Mandal, M., Kundu, S., Ghosh, S.K., and Pal, T. (2004) Micelle-mediated UV-photoactivation route for the evolution of Pd_{core}–Au_{shell} and Pd_{core}–Ag_{shell} bimetallics from photogenerated Pd nanoparticles. *J. Photochem. Photobiol., A*, **167** (1), 17–22.
- 93 Zhang, Z., Zhang, X., Xin, Z., Deng, M., Wen, Y., and Song, Y. (2013) Controlled inkjetting of a conductive pattern of silver nanoparticles based on coffee-ring effect. *Adv. Mater.*, **25** (46), 6714–6718.
- 94 Deng, D., Cheng, Y., Jin, Y., Qi, T., and Xiao, F. (2012) Antioxidative effect of lactic acid-stabilized copper nanoparticles prepared in aqueous solution. *J. Mater. Chem.*, **22** (45), 23989–23995.
- 95 Kang, S.W. and Kang, Y.S. (2011) Silver nanoparticles stabilized by crosslinked poly(vinyl pyrrolidone) and its application for facilitated olefin transport. *J. Colloid Interface Sci.*, **353** (1), 83–86.
- 96 Jeong, S., Woo, K., Kim, D., Lim, S., Kim, J.S., Shin, H., Xia, Y., and Moon, J. (2008) Controlling the thickness of the surface oxide layer on Cu nanoparticles for the fabrication of conductive structures by ink-jet printing. *Adv. Funct. Mater.*, **18** (5), 679–686.
- 97 Lee, H.-H., Chou, K., and Huang, K.-C. (2005) Inkjet printing of nanosized silver colloids. *Nanotechnology*, **16** (10), 2436–2441.
- 98 Patakfalvi, R., Papp, S., and Dékány, I. (2007) The kinetics of homogeneous nucleation of silver nanoparticles stabilized by polymers. *J. Nanopart. Res.*, **9** (3), 353–364.
- 99 Sarkar, A., Mukherjee, T., and Kapoor, S. (2008) PVP-stabilized copper nanoparticles: A reusable catalyst for “click” reaction between terminal alkynes and azides in nonaqueous solvents. *J. Phys. Chem. C*, **112** (9), 3334–3340.
- 100 Woo, K., Kim, D., Kim, J.S., Lim, S., and Moon, J. (2009) Ink-jet printing of Cu-Ag based highly conductive tracks on a transparent substrate. *Langmuir*, **25** (1), 429–433.
- 101 Teranishi, T. and Miyake, M. (1998) Size control of palladium nanoparticles and their crystal structures. *Chem. Mater.*, **10** (2), 594–600.
- 102 Patakfalvi, R., Virányi, Z., and Dékány, I. (2004) Kinetics of silver nanoparticle growth in aqueous polymer solutions. *Colloid. Polym. Sci.*, **283** (3), 299–305.
- 103 Hirai, H., Wakabayashi, H., and Komiyama, M. (1986) Preparation of polymer-protected colloidal dispersions of copper. *Bull. Chem. Soc. Jpn.*, **59** (2), 367–372.

- 104 Khanna, P.K., Gaikwad, S., Adhyapak, P.V., Singh, N., and Marimuthu, R. (2007) Synthesis and characterization of copper nanoparticles. *Mater. Lett.*, **61** (25), 4711–4714.
- 105 Kosmala, A., Wright, R., Zhang, Q., and Kirby, P. (2011) Synthesis of silver nano particles and fabrication of aqueous Ag inks for inkjet printing. *Mater. Chem. Phys.*, **129** (3), 1075–1080.
- 106 Ryu, B.-H., Choi, Y., Park, H.-S., Byun, J.-H., Kong, K., Lee, J.-O., and Chang, H. (2005) Synthesis of highly concentrated silver nanosol and its application to inkjet printing. *Colloids Surf., A*, **270–271**, 345–351.
- 107 Grouchko, M., Kamyshny, A., Ben-Ami, K., and Magdassi, S. (2009) Synthesis of copper nanoparticles catalyzed by pre-formed silver nanoparticles. *J. Nanopart. Res.*, **11** (3), 713–716.
- 108 Grouchko, M., Kamyshny, A., and Magdassi, S. (2009) Formation of air-stable copper-silver core-shell nanoparticles for inkjet printing. *J. Mater. Chem.*, **19** (19), 3057–3062.
- 109 Grouchko, M., Kamyshny, A., Mihailescu, C.F., Anghel, D.F., and Magdassi, S. (2011) Conductive inks with a "built-in" mechanism that enables sintering at room temperature. *ACS Nano*, **5** (4), 3354–3359.
- 110 Ahn, B.Y., Walker, S.B., Slimmer, S.C., Russo, A., Gupta, A., Kranz, S., Duoss, E.B., Malkowski, T.F., and Lewis, J.A. (2011) Planar and three-dimensional printing of conductive inks. *J. Vis. Exp.*, **58**, e3189(1–8).
- 111 Zhang, Z. and Zhu, W. (2014) Controllable fabrication of a flexible transparent metallic grid conductor based on the coffee ring effect. *J. Mater. Chem. C*, **2** (45), 9587–9591.
- 112 Magdassi, S., Bassa, A., Vinetsky, Y., and Kamyshny, A. (2003) Silver nanoparticles as pigments for water-based ink-jet inks. *Chem. Mater.*, **15** (11), 2208–2217.
- 113 Chen, H., Wang, Y., Wang, Y., Dong, S., and Wang, E. (2006) One-step preparation and characterization of PDDA-protected gold nanoparticles. *Polymer*, **47** (2), 763–766.
- 114 Sun, X., Dong, S., and Wang, E. (2004) One-step synthesis and characterization of polyelectrolyte-protected gold nanoparticles through a thermal process. *Polymer*, **45** (7), 2181–2184.
- 115 Suber, L., Sondi, I., Matijević, E., and Goia, D.V. (2005) Preparation and the mechanisms of formation of silver particles of different morphologies in homogeneous solutions. *J. Colloid Interface Sci.*, **288** (2), 489–495.
- 116 Magdassi, S., Kamyshny, A., Aviezer, S. and Grouchko, M. (2011) Aqueous-based dispersions of metal nanoparticles. US Patent Appl. US 2012/0241693, filed June 5, 2012.
- 117 Daniel, M.-C. and Astruc, D. (2004) Gold nanoparticles: Assembly, supramolecular chemistry, quantum-size-related properties, and applications towards biology, catalysis, and nanotechnology. *Chem. Rev.*, **104** (1), 293–346.
- 118 Huang, D., Liao, F., Moles, S., Redinger, D., and Subramanian, V. (2003) Plastic-compatible low resistance printable gold nanoparticle conductors for flexible electronics. *J. Electrochem. Soc.*, **150** (7), G412–G417.

- 119 Wu, Y., Li, Y., Liu, P., Gardner, S., and Ong, B.S. (2006) Studies of gold nanoparticles as precursors to printed conductive features for thin-film transistors. *Chem. Mater.*, **18** (19), 4627–4632.
- 120 Määttänen, A., Ihalainen, P., Pulkkinen, P., Wang, S., Tenhu, H., and Peltonen, J. (2012) Inkjet-printed gold electrodes on paper: Characterization and functionalization. *ACS Appl. Mater. Interfaces*, **4** (2), 955–964.
- 121 Bishop, P.T., Ashfield, L.J., Berzins, A., Boardman, A., Buche, V., Cookson, J., Gordon, R.J., Salcianu, C., and Sutton, P.A. (2010) Printer gold for electronic applications. *Gold Bull.*, **43** (3), 181–188.
- 122 Jang, S., Cho, H., Kang, S., Oh, S., and Kim, D. (2011) Inkjet-printed nanoparticulate patterns for surface finish in electronic package. *Appl. Phys. A*, **105** (3), 685–690.
- 123 Campbell, T., Kalia, R.K., Nakano, A., and Vashishta, P. (1999) Dynamics of oxidation of aluminum nanoclusters using variable charge molecular-dynamics simulations on parallel computers. *Phys. Rev. Lett.*, **82** (24), 4866–4869.
- 124 Foley, T.J., Johnson, C.E., and Higa, K.T. (2005) Inhibition of oxide formation on aluminum nanoparticles by transition metal coating. *Chem. Mater.*, **17** (16), 4086–4091.
- 125 Wu, C., Mosher, B.P., and Zeng, T. (2006) One-step green route to narrowly dispersed copper nanocrystals. *J. Nanopart. Res.*, **8** (6), 965–969.
- 126 Wu, C.-J., Chen, S.-M., Sheng, Y.-J., and Tsao, H.-K. (2014) Anti-oxidative copper nanoparticles and their conductive assembly sintered at room temperature. *J. Taiwan Inst. Chem. Eng.*, **45** (5), 2719–2724.
- 127 Carrol, K.J., Reveles, J.U., Shultz, M.D., Khanna, S.N., and Carpenter, E.E. (2011) Preparation of elemental Cu and Ni nanoparticles by the polyol method: An experimental and theoretical approach. *J. Phys. Chem. C*, **115** (6), 2656–2664.
- 128 Wang, Y., Chen, P., and Liu, M. (2006) synthesis of well-defined copper nanocubes by a one-pot solution process. *Nanotechnology*, **17** (24), 6000–6006.
- 129 Woo, K., Bae, C., Jeong, Y., Kim, D., and Moon, J. (2010) Inkjet printed Cu source-drain electrodes for solution-deposited thin film transistors. *J. Mater. Chem.*, **20** (19), 3877–3882.
- 130 Li, W., Li, W., Wei, J., Tan, J., and Chen, M. (2014) Preparation of conductive Cu patterns by directly writing using nano-Cu ink. *Mater. Chem. Phys.*, **146** (1), 82–87.
- 131 Tsai, C.-Y., Chang, W.-C., Chen, G.-L., Chung, C.-H., Liang, J.-X., Ma, W.-Y., and Yang, T.-N. (2015) A study of the preparation and properties of antioxidative copper inks with high electrical conductivity. *Nanoscale Res. Lett.*, **10**, 357 (17).
- 132 Song, X., Sun, S., Zhang, W., and Yin, Z. (2004) A method for the synthesis of spherical copper nanoparticles in the organic phase. *J. Colloid Interface Sci.*, **273** (2), 463–469.
- 133 Mott, D., Galkowski, J., Wang, L., Luo, J., and Zhong, C.-J. (2007) Synthesis of size-controlled and shaped copper nanoparticles. *Langmuir*, **23** (10), 5740–5745.

- 134 Jeong, S., Lee, S.H., Jo, Y., Lee, S.S., Seo, Y.-H., Ahn, B.W., Kim, G., Jang, G.-E., Park, J.-U., Ryu, B.-H., and Choi, Y. (2013) Air-stable, surface-oxide free Cu nanoparticles for highly conductive Cu ink and their application to printed graphene transistors. *J. Mater. Chem. C*, **1** (15), 2704–2710.
- 135 Kanninen, P., Johans, C., Merta, J., and Kontturi, K. (2008) Influence of ligand structure on the stability and oxidation of copper nanoparticles. *J. Colloid Interface Sci.*, **318** (1), 88–95.
- 136 Oh, S.-J., Jo, Y., Lee, E.J., Lee, S.S., Kang, Y.H., Jeon, H.-J., Cho, S.Y., Park, J.-S., Seo, Y.-H., Ryu, B.-H., Choi, Y., and Jeong, S. (2015) Ambient atmosphere-processable, printable Cu electrodes for flexible device applications: Structural welding on a millisecond timescale of surface oxide-free Cu nanoparticles. *Nanoscale*, **7** (9), 3997–4004.
- 137 Ang, T.P., Wee, T.S.A., and Chin, W.S. (2004) Three-dimensional self-assembled monolayer (3D SAM) of n-alkanethiols on copper nanoclusters. *J. Phys. Chem. B*, **108** (30), 11001–11010.
- 138 Kwon, J., Park, S., Haque, M.M., Kim, Y.-S., and Lee, C.S. (2012) Study of sintering behavior of vapor forms of 1-octanethiol coated copper nanoparticles for application to ink-jet technology. *J. Nanosci. Nanotechnol.*, **12** (4), 3434–3437.
- 139 Park, B.K., Kim, D., Jeong, S., Moon, J., and Kim, J.S. (2007) Direct writing of copper conductive patterns by ink-jet printing. *Thin Solid Films*, **515** (19), 7706–7711.
- 140 Kim, I., Kim, Y., Woo, K., Ryu, E.-H., Yon, K.-Y., Cao, G., and Moon, J. (2013) Synthesis of oxidation-resistant core-shell copper nanoparticles. *RSC Adv.*, **3** (35), 15169–15177.
- 141 Leuchinger, N.A., Athanassiou, E.K., and Stark, W.J. (2008) Graphene-stabilized copper nanoparticles as an air-stable substitute for silver and gold in low-cost ink-jet printable electronics. *Nanotechnology*, **19** (44), 445201(1–6).
- 142 Lee, W.-R., Kim, M.G., Choi, J.-R., Park, J.-I., Ko, S.J., Oh, S.J., and Cheon, J. (2005) Redox-transmetalation process as a generalized synthetic strategy for core-shell magnetic nanoparticles. *J. Am. Chem. Soc.*, **127** (46), 16090–16097.
- 143 Chen, D., Li, J., Shi, C., Du, X., Zhao, N., Sheng, J., and Liu, S. (2007) Properties of core-shell Ni-Au nanoparticles synthesized through a redox-transmetalation method in reverse microemulsion. *Chem. Mater.*, **19** (14), 3399–3405.
- 144 Lee, C., Kim, N.R., Koo, J., Lee, Y.J., and Lee, H.M. (2015) Cu-Ag core-shell nanoparticles with enhanced oxidation stability for printed electronics. *Nanotechnology*, **26** (45), 455601(1–9).
- 145 Muzikansky, A., Nanikashvili, P., Grinblat, J., and Zitoun, D. (2013) Ag dewetting in Cu@Ag monodisperse core-shell nanoparticles. *J. Phys. Chem.*, **117** (6), 3093–3100.
- 146 Kim, C.K., Lee, G.-J., Lee, M.K., and Rhee, C.K. (2014) A novel method to prepare Cu@Ag core-shell nanoparticles for printed flexible electronics. *Powder Technol.*, **263**, 1–6.

- 147 Miyakawa, M., Hiyoshi, N., Nishioka, M., Koda, H., Sato, K., Miyazawa, A., and Suzuki, T.M. (2014) Continuous syntheses of Pd@Pt and Cu@Ag core-shell nanoparticles using microwave-assisted core particle formation coupled with galvanic metal displacement. *Nanoscale*, **6** (15), 8720–8725.
- 148 Chee, S.-S. and Lee, J.-H. (2014) Preparation and oxidation behavior of Ag-coated Cu nanoparticles less than 20 nm in size. *J. Mater. Chem. C*, **2** (27), 5372–5381.
- 149 Hong, S. and Kim, N. (2015) Synthesis of 3D printable Cu–Ag core-shell materials: Kinetics of CuO film removal. *J. Electron. Mater.*, **44** (3), 823–830.
- 150 Chen, Z., Mochizuki, D., Maitani, M.M., and Wada, Y. (2013) Facile synthesis of bimetallic Cu–Ag nanoparticles under microwave irradiation and their oxidation resistance. *Nanotechnology*, **24** (26), 265602(1–9).
- 151 Nir, M.M., Zamir, D., Haymov, I., Ben-Asher, L., Cohen, O., Faulkner, B., and De La Vega, F. (2010) Electrically conductive inks for inkjet printing, in *Chemistry of Inkjet Inks* (ed. S. Magdassi), World Scientific, New Jersey, London, Singapore, pp. 225–254.
- 152 Sondi, I., Goia, D.V., and Matijević, E. (2003) Preparation of highly concentrated stable dispersions of uniform silver nanoparticles. *J. Colloid Interface Sci.*, **260** (1), 75–81.
- 153 Lee, K.J., Jun, B.H., Kim, T.H., and Joung, J. (2006) Direct synthesis and inkjetting of silver nanocrystals toward printed electronics. *Nanotechnology*, **17** (9), 2424–2428.
- 154 Balantrapu, K. and Goia, D.V. (2009) Silver nanoparticles for printable electronics and biological applications. *J. Mater. Res.*, **24** (9), 2828–2836.
- 155 Anto, B.T., Sivaramakrishnan, S., Chua, L.-L., and Ho, P.K.H. (2010) Hydrophilic sparse ionic monolayer-protected metal nanoparticles: Highly concentrated nano-Au and nano-Ag “inks” that can be sintered to near-bulk conductivity at 150 °C. *Adv. Funct. Mater.*, **20** (2), 296–303.
- 156 Kim, D. and Moon, J. (2005) Highly conductive ink jet printed films of nanosilver particles for printable electronics. *Electrochem. Solid-State Lett.*, **8** (11), J30–J33.
- 157 Bai, J.G., Creehan, K.D., and Kuhn, H.A. (2007) Inkjet printable nanosilver suspensions for enhanced sintering quality in rapid manufacturing. *Nanotechnology*, **18** (18), 185701(1–5).
- 158 Ummartyotin, S., Bunnak, N., Juntaro, J., Sain, M., and Manuspiya, H. (2012) Synthesis of colloidal silver nanoparticles for printed electronics. *C. R. Chim.*, **15** (6), 539–544.
- 159 Kim, T.H., Seo, Y.K., Kim, D.H., Jun, B.H. and Kim, S.E. (2011) Metal ink composition and method for forming the metal line using the same, and conductive pattern formed by using the metal ink composition. US Patent Appl. US 2011/0318541, filed Sept. 29, 2010.
- 160 Zhang, Z., Zhang, X., Xin, Z., Deng, M., Wen, Y., and Song, Y. (2011) Synthesis of monodisperse silver nanoparticles for ink-jet printed flexible electronics. *Nanotechnology*, **22** (42), 425601(1–8).
- 161 Subramanian, V., Huang, D., Volkman, S. and Liao, F. (2007) Method of forming conductors at low temperatures using metallic nanocrystals and product. US Patent Appl. US 2007/0175296, filed Aug. 15, 2005.

- 162 Toshima, N. and Yonezawa, T. (1998) Bimetallic nanoparticles – novel materials for chemical and physical applications. *New J. Chem.*, **22** (11), 1179–1201.
- 163 Mafune, F., Kohno, J., Takeda, Y., Kondow, T., and Sawabe, H. (2000) Formation and size control of silver nanoparticles by laser ablation in aqueous solution. *J. Phys. Chem. B*, **104** (39), 9111–9117.
- 164 Chen, Y.-H. and Yeh, C.-S. (2002) Laser ablation method: Use of surfactants to form the dispersed Ag nanoparticles. *Colloids Surf., A*, **197** (1–3), 133–139.
- 165 Keskinen, J., Ruuskanen, P., Karttunen, M., and Hannula, S.-P. (2001) Synthesis of silver powder using a mechanochemical process. *Appl. Organomet. Chem.*, **15** (5), 393–395.
- 166 Lee, J., Ahn, J.-G., Tung, L.M., Kim, D.-J., Kim, C.-O., Chung, H.S., and Kim, B.-G. (2006) Preparation of Ag powders by mechanochemical reaction in AgCl-Cu system. *TMS Lett.*, **3** (2), 41–42.
- 167 Sanches-Romaguera, V., Wünscher, S., Turki, B.M., Abbel, R., Barbosa, S., Tate, D.J., Oyeka, D., Batchelor, J.C., Parker, E.A., Schubert, U.S., and Yeates, S.G. (2015) Inkjet printed paper based frequency selective surfaces and skin mounted RFID tags: The interrelation between silver nanoparticle ink, paper substrate and low temperature sintering technique. *J. Mater. Chem. C*, **3** (9), 2132–2140.
- 168 Natsuki, J., Natsuki, T., and Abe, T. (2013) Low molecular weight compounds as effective dispersing agents in the formation of colloidal silver nanoparticles. *J. Nanopart. Res.*, **15** (3), 1483(1–8).
- 169 Chung, J., Bieri, N.R., Ko, S., Grigoropoulos, C.P., and Poulikakos, D. (2004) In-tandem deposition and sintering of printed gold nanoparticle inks induced by continuous Gaussian laser irradiation. *Appl. Phys. A*, **79** (4–6), 1259–1261.
- 170 Szczech, J.B., Megaridis, C.M., Zhang, J., and Gamota, D.R. (2004) Ink jet processing of metallic nanoparticle suspension for electronic circuitry fabrication. *Microscale Thermophys. Eng.*, **8** (4), 327–339.
- 171 Itoh, D., Izumitani, A., Hata, N., Matsuba, Y., Murata, K. and Yokoyama, H. (2015) Metal nanoparticle dispersion usable for ejection in the form of fine droplets to be applied in the layered shape. US Patent 9,006,296, filed Sept. 10, 2004 and issued Apr. 14, 2015.
- 172 Gamerith, S., Klug, A., Scheiber, H., Scherf, U., Moderegger, E., and List, E.J.W. (2007) Direct ink-jet printing of Ag-Cu nanoparticle and Ag-precursor based electrodes for OFET applications. *Adv. Funct. Mater.*, **17** (16), 3111–3118.
- 173 Fuller, S.B., Wilhelm, E.J., and Jacobson, J.M. (2002) Ink-jet printed nanoparticle microelectromechanical systems. *J. Microelectromech. Syst.*, **11** (1), 54–60.
- 174 Tseng, C.-C., Chang, C.-P., Sung, Y., Chen, Y.-C., and Ger, M.-D. (2009) A novel method to produce Pd nanoparticle ink for ink-jet printing technology. *Colloids Surf., A*, **339** (1–3), 206–210.

- 175 Okada, I. and Shimada, K. (2009) Metallic colloidal solution and inkjet-use metallic ink. US Patent 7,608,203, filed Aug. 21, 2008 and issued Oct. 27, 2009.
- 176 Kim, D., Jeong, S., Park, B.K., and Moon, J. (2006) Direct writing of silver conductive patterns. Improvement of film morphology and conductance by controlling solvent compositions. *Appl. Phys. Lett.*, **89** (26), 264101(1–3).
- 177 Li, X., Li, Y., Laxton, P.B., Roundhill, D.M. and Arimura, H. (2013) Additives and modifiers for solvent- and water-based metallic conductive inks. US Patent 8,506,849, filed Feb. 24, 2009 and issued Aug. 13, 2013.
- 178 Park, B.K., Jeong, S., Kim, D., Moon, J., Lim, S., and Kim, J.S. (2007) Synthesis and size control of monodisperse copper nanoparticles by polyol method. *J. Colloid Interface Sci.*, **311** (2), 417–424.
- 179 Perelaer, J., De Laat, A.W.M., Hendriks, C.E., and Schubert, U.S. (2008) Inkjet-printed silver tracks: Low temperature curing and thermal stability investigation. *J. Mater. Chem.*, **18** (27), 3209–3215.
- 180 Huang, Q., Shen, W., Xu, Q., Tan, R., and Song, W. (2014) Properties of polyacrylic acid-coated silver nanoparticle ink for inkjet printing conductive tracks on paper with high conductivity. *Mater. Chem. Phys.*, **147** (3), 550–556.
- 181 Perelaer, J. (2012) Postprinting processes for inorganic inks for plastic electronics applications, in *Inkjet-Based Micromanufacturing* (eds J.P. Korvink, P.J. Smith, and D.-Y. Shin), Wiley-VCH, Weinheim, Germany, pp. 111–125.
- 182 Dick, K., Dhanasekaran, T., Zhang, Z., and Meisel, D. (2002) Size-dependent melting of silica-encapsulated gold nanoparticles. *J. Am. Chem. Soc.*, **124** (10), 2312–2317.
- 183 Grouchko, M., Roitman, P., Zhu, X., Popov, I., Kamysny, A., Su, H., and Magdassi, S. (2014) Merging of metal nanoparticles driven by selective wettability of silver nanostructures. *Nat. Commun.*, **5**, 2994(1–5).
- 184 Buffat, P. and Borel, J.-P. (1976) Size effect on the melting temperature of gold particles. *Phys. Rev. A*, **13** (6), 2287–2298.
- 185 Scandurra, A., Indelli, G.F., Spartà, N.G., Galliano, F., Ravesi, S., and Pignataro, S. (2010) Low-temperature sintered conductive silver patterns obtained by inkjet printing for plastic electronics. *Surf. Interface Anal.*, **42** (6–7), 1163–1167.
- 186 Vaseem, M., Lee, K.M., Hong, A.-R., and Hahn, Y.-B. (2012) Inkjet printed fractal-connected electrodes with silver nanoparticle ink. *ACS Appl. Mater. Interfaces*, **4** (6), 3300–3307.
- 187 Hwang, J.-Y. and Moon, S.-J. (2013) The characteristic variations of inkjet-printed silver nanoparticle ink during furnace sintering. *J. Nanosci. Nanotechnol.*, **13** (9), 6145–6149.
- 188 Halonen, E., Viiru, T., Ostman, K., Cabezas, A.L., and Mantysalo, M. (2013) Oven sintering process for inkjet printed Ag nanoparticles ink. *IEEE Trans. Compon., Packag., Manuf. Technol.*, **3** (2), 350–356.
- 189 Kang, J.S., Kim, H.S., Ryu, J., Hahn, H.T., Jang, S., and Joung, J.W. (2010) Inkjet printed electronics using copper nanoparticle ink. *J. Mater. Sci.: Mater. Electron.*, **21** (11), 1213–1220.

- 190 Kang, J.S., Ryu, J., Kim, H.S., and Hahn, H.T. (2011) Sintering of inkjet-printed silver nanoparticles at room temperature using intense pulsed light. *J. Electron. Mater.*, **40** (11), 2268–2277.
- 191 Tobjörk, D., Aarnio, H., Pulkkinen, P., Bollström, R., Määttä, A., Ihalainen, P., Mäkelä, T., Peltonen, J., Toivakka, M., Tenhu, H., and Österbacka, R. (2012) IR-sintering of inkjet printed metal-nanoparticles on paper. *Thin Solid Films*, **520** (7), 2949–2955.
- 192 Lee, D.G., Kim, D.K., Moon, Y.J., and Moon, S.-J. (2013) Effect of laser-induced temperature field on the characteristics of laser-sintered silver nanoparticle ink. *Nanotechnology*, **24** (26), 265702(1–9).
- 193 Bieri, N.R., Chung, J., Poulikakos, D., and Grigoropoulos, C.P. (2004) Manufacturing on nanoscale thickness gold lines by laser curing of a discretely deposited nanoparticle suspension. *Superlattices Microstruct.*, **35** (3–6), 437–444.
- 194 Dharmadasa, R., Jha, M., Amos, D.A., and Druffel, T. (2013) Room temperature synthesis of a copper ink for the intense pulsed light sintering of conductive copper films. *ACS Appl. Mater. Interfaces*, **5** (24), 13227–13234.
- 195 Joo, S.-J., Hwang, S.-J., and Kim, H.-S. (2014) Highly conductive copper nano/microparticles ink via flash light sintering for printed electronics. *Nanotechnology*, **25** (26), 265601(1–11).
- 196 Zenou, M., Ermak, O., Saar, A., and Kotler, Z. (2014) Laser sintering of copper nanoparticles. *J. Phys. D: Appl. Phys.*, **47** (2), 025501(1–11).
- 197 Niittynen, J., Abbel, R., Mäntysalo, M., Perelaer, J., Schubert, U.S., and Lupo, D. (2014) Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink. *Thin Solid Films*, **556**, 452–459.
- 198 Liana, D.D., Rabuse, B., Wieczorek, L., Baxter, G.R., Chuah, K., Gooding, J.J., and Chow, E. (2013) Sintered gold nanoparticles as an electrode material for paper-based electrochemical sensors. *RSC Adv.*, **3** (23), 8683–8691.
- 199 Kim, H.-S., Dhage, S.R., Shim, D.-E., and Hahn, H.T. (2009) Intense pulsed light sintering of copper nanoink for printed electronics. *Appl. Phys. A*, **97** (4), 791–798.
- 200 Ryu, J., Kim, H.-S., and Hahn, H.T. (2011) Reactive sintering of copper nanoparticles using intense pulsed light for printed electronics. *J. Electron. Mater.*, **40** (1), 42–49.
- 201 Park, S.-H., Jang, S., Lee, D.-J., Oh, J., and Kim, H.-S. (2013) Two-step light flash sintering process for crack-free inkjet-printed Ag films. *J. Micromech. Microeng.*, **23** (1), 015013(1–9).
- 202 Hwang, H.-J., Chung, W.-H., and Kim, H.-S. (2012) In situ monitoring of flash-light sintering of copper nanoparticle ink for printed electronics. *Nanotechnology*, **23** (48), 485205(1–9).
- 203 Han, W.-S., Hong, J.-M., Kim, H.-S., and Song, Y.-W. (2011) Multi-pulse white light sintering of printed copper nanoinks. *Nanotechnology*, **22** (39), 395705(1–6).
- 204 Park, S.-H. and Kim, H.-S. (2014) Flash light sintering of nickel nanoparticles for printed electronics. *Thin Solid Films*, **550**, 575–581.

- 205 Chung, W.H., Hwang, H.-J., Lee, S.-H., and Kim, H.-S. (2013) *In situ* monitoring of a flash light sintering process using silver nano-ink for producing flexible electronics. *Nanotechnology*, **24** (3), 035202(1–8).
- 206 Lim, S., Joyce, M., Fleming, P.D., Aijazi, A.T., and Atashbar, M. (2013) Inkjet printing and sintering of nano-copper ink. *J. Imaging Sci. Technol.*, **57** (5), 050506(1–7).
- 207 Jo, Y., Oh, S.-J., Lee, S.S., Seo, Y.-H., Ryu, B.-H., Moon, J., Choi, Y., and Jeong, S. (2014) Extremely flexible, printable Ag conductive features on PET and paper substrates *via* continuous millisecond photonic sintering in a large area. *J. Mater. Chem. C*, **2** (45), 9746–9753.
- 208 Perelaer, J., Abbel, R., Wünscher, S., Jani, R., van Lammeren, T., and Schubert, U.S. (2012) Roll-to-roll compatible sintering of inkjet printed features by photonic and microwave exposure: From non-conductive ink to 40% bulk silver conductivity in less than 15 seconds. *Adv. Mater.*, **24** (19), 2620–2625.
- 209 Yung, K.C., Gu, X., Lee, C.P., and Choy, H.S. (2010) Inkjet printing and camera flash sintering of silver tracks on different substrates. *J. Mater. Process. Technol.*, **210** (15), 2268–2272.
- 210 Kumpulainen, T., Pekkanen, J., Valkama, J., Laakso, J., Tuokko, R., and Mäntysalo, M. (2011) Low temperature nanoparticle sintering with continuous wave and pulse lasers. *Opt. Laser Technol.*, **43** (3), 570–576.
- 211 Joo, M., Lee, B., Jeong, S., and Lee, M. (2012) Comparative studies on thermal and laser sintering for highly conductive Cu films printable on plastic substrate. *Thin Solid Films*, **520** (7), 2878–2883.
- 212 Ko, S.H., Pan, H., Grigoropoulos, C.P., Luscombe, C.K., Fréchet, J.M.J., and Poulidakos, D. (2007) All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles. *Nanotechnology*, **18** (34), 345202(1–8).
- 213 Cherrington, M., Claypole, T.C., Deganello, D., Mabbett, I., Watson, T., and Worsley, D. (2011) Ultrafast near-infrared sintering of a slot-die coated nano-silver conducting ink. *J. Mater. Chem.*, **21** (21), 7562–7564.
- 214 Denneulin, A., Blayo, A., Neuman, C., and Bras, J. (2011) Infra-red assisted sintering of inkjet printed silver tracks on paper substrates. *J. Nanopart. Res.*, **13** (9), 3815–3823.
- 215 Perelaer, J. and Schubert, U.S. (2013) Novel approaches for low temperature sintering of inkjet-printed inorganic nanoparticles for roll-to-roll (R2R) applications. *J. Mater. Res.*, **28** (4), 564–573.
- 216 Reinhold, I., Hendriks, C.E., Eckardt, R., Kranenburg, J.M., Perelaer, J., Baumann, R.R., and Schubert, U.S. (2009) Argon plasma sintering of inkjet printed silver tracks on polymer substrates. *J. Mater. Chem.*, **19** (21), 3384–3388.
- 217 Perelaer, J., Jani, R., Grouchko, M., Kamyshtny, A., Magdassi, S., and Schubert, U.S. (2012) Plasma and microwave flash sintering of a tailored silver nanoparticle ink, yielding 60% bulk conductivity on cost-effective polymer foils. *Adv. Mater.*, **24** (29), 3993–3998.

- 218 Wolf, M., Perelaer, J., Stumpf, S., Bollen, D., Kriebel, F., and Schubert, U.S. (2013) Rapid low-pressure plasma sintering of inkjet-printed silver nanoparticles for RFID antennas. *J. Mater. Res.*, **28** (9), 1254–1261.
- 219 Ma, S., Bromberg, V., Liu, L., Egitto, F.D., Chiarot, P.R., and Singler, T.J. (2014) Low temperature plasma sintering of silver nanoparticles. *Appl. Surf. Sci.*, **293**, 207–215.
- 220 Wünscher, S., Stumpf, S., Teichler, A., Rabst, O., Perelaer, J., Beckert, E., and Schubert, U.S. (2012) Localized atmospheric plasma sintering of inkjet printed silver nanoparticles. *J. Mater. Chem.*, **22** (47), 24569–24576.
- 221 Kim, K.-S., Bang, J.-O., Choa, Y.-H., and Jung, S.-B. (2013) The characteristics of Cu nanopaste sintered by atmospheric-pressure plasma. *Microelectron. Eng.*, **107**, 121–124.
- 222 Perelaer, J., de Gans, B.-J., and Schubert, U.S. (2006) Inkjet printing and microwave sintering of conductive silver tracks. *Adv. Mater.*, **18** (16), 2101–2104.
- 223 Perelaer, J., Klokkenburg, M., Hendriks, C.E., and Schubert, U.S. (2009) Microwave flash sintering of inkjet-printed silver tracks on polymer substrates. *Adv. Mater.*, **21** (47), 4830–4834.
- 224 Allen, M.L., Aronniemi, M., Mattila, T., Alastalo, A., Ojanperä, K., Suhonen, M., and Seppä, H. (2008) Electrical sintering of nanoparticle structures. *Nanotechnology*, **19** (17), 175201(1–4).
- 225 Moon, S.-J. (2013) The effect of temperature on the electrical properties of inkjet-printed silver nanoparticle ink during electrical sintering. *J. Nanosci. Nanotechnol.*, **13** (9), 6174–6178.
- 226 Allen, M., Alastalo, A., Suhonen, M., Mattila, T., Leppäniemi, J., and Seppä, H. (2011) Contactless electrical sintering of silver nanoparticles on flexible substrates. *IEEE Trans. Microwave Theory Tech.*, **59** (5), 1419–14229.
- 227 Coutts, M.J., Cortie, M.B., Ford, M.J., and McDonagh, A.M. (2009) Rapid and controllable sintering of gold nanoparticle inks at room temperature using a chemical agent. *J. Phys. Chem. C*, **113** (4), 1325–1328.
- 228 Wakuda, D., Hatamura, M., and Suganuma, K. (2007) Novel method for room temperature sintering of Ag nanoparticles paste in air. *Chem. Phys. Lett.*, **441** (4–6), 305–308.
- 229 Magdassi, S., Grouchko, M., Berezin, O., and Kamyshny, A. (2010) Triggering the sintering of silver nanoparticles at room temperature. *ACS Nano*, **4** (4), 1943–1948.
- 230 Magdassi, S., Grouchko, M. and Kamyshny, A. (2009) *Conductive Ink-Jet Inks for Plastic Electronics: Air Stable Copper Nanoparticles and Room Temperature Sintering*. NIP25: Proc. Intern. Conf. Digital Printing Technol. Digital Fabrication, Sept. 20–24, 2009, Louisville, Kentucky, USA, pp. 611–613.
- 231 Zapka, W., Voit, W., Loderer, C. and Lang, P. (2008) *Low Temperature Chemical Post-Treatment of Inkjet Printed Nano-particle Silver Inks*. NIP24: Proc. Intern. Conf. Digital Printing Technol. Digital Fabrication, Sept. 8–12, 2008, Pittsburgh, Pennsylvania, USA, pp. 906–911.
- 232 Olkkonen, J., Leppäniemi, J., Mattila, T., and Eiroma, K. (2014) Sintering of inkjet printed silver tracks with boiling salt water. *J. Mater. Chem. C*, **2** (18), 3577–3582.

- 233 Tang, Y., He, W., Zhou, G., Wang, S., Yang, X., Tao, Z., and Zhou, J. (2012) A new approach causing the patterns fabricated by silver nanoparticles to be conductive without sintering. *Nanotechnology*, **23** (35), 355304(1–6).
- 234 Layani, M., Grouchko, M., Shemesh, S., and Magdassi, S. (2012) Conductive patterns on plastic substrates by sequential inkjet printing of silver nanoparticles and electrolyte sintering solutions. *J. Mater. Chem.*, **22** (29), 14349–14352.
- 235 Layani, M. and Magdassi, S. (2011) Flexible transparent conductive coatings by combining self-assembly with sintering of silver nanoparticles performed at room temperature. *J. Mater. Chem.*, **21** (39), 15378–15382.
- 236 Lewis, J.A. (2006) Direct ink writing of 3D functional materials. *Adv. Funct. Mater.*, **16** (17), 2193–2204.
- 237 Napadensky, E. (2010) Inkjet 3D printing, in *Chemistry of Inkjet Inks* (ed. S. Magdassi), World Scientific, New Jersey, London, Singapore, pp. 255–267.
- 238 Sanchez-Romaguera, V., Madec, M.-B., and Yeates, S.G. (2008) Inkjet printing of 3D metal-insulator-metal crossovers. *React. Funct. Polym.*, **68** (6), 1052–1058.
- 239 Kullmann, C., Schirmer, N.C., Lee, M.-T., Ko, S.H., Hotz, N., Grigoropoulos, C.P., and Poulikakos, D. (2012) 3D micro-structures by piezoelectric inkjet printing of gold nanofluids. *J. Micromech. Microeng.*, **22** (5), 055022(1–11).
- 240 Layani, M., Cooperstein, I., and Magdassi, S. (2013) UV crosslinkable emulsions with silver nanoparticles for inkjet printing of conductive 3D structures. *J. Mater. Chem. C*, **1** (19), 3244–3249.
- 241 Sadie, J.A. and Subramanian, V. (2014) Three-dimensional inkjet-printed interconnects using functional metallic nanoparticle inks. *Adv. Funct. Mater.*, **24** (43), 6834–6842.
- 242 Haque, R.I., Ogam, E., Loussert, C., Benaben, P., and Boddaert, X. (2015) Fabrication of capacitive acoustic resonators combining 3D printing and 2D inkjet printing techniques. *Sensors*, **15** (10), 26018–26038.
- 243 An, B.W., Kim, K., Lee, H., Kim, S.-Y., Shim, Y., Lee, D.-Y., Song, J.Y., and Park, J.-U. (2015) High-resolution printing of 3D structures using an electrohydrodynamic inkjet with multiple functional inks. *Adv. Mater.*, **27** (29), 4322–4328.
- 244 Ko, S.H., Chung, J., Hotz, N., Nam, K.H., and Grigoropoulos, C.P. (2010) Metal nanoparticle direct inkjet printing for low-temperature 3D micro metal structure fabrication. *J. Micromech. Microeng.*, **20** (12), 125010(1–7).
- 245 Sangermano, M., Chiolerio, A., Marti, G., and Martino, P. (2013) UV-curved acrylic conductive inks for microelectronic devices. *Macromol. Mater. Eng.*, **298** (6), 607–611.
- 246 Cooperstein, I., Layani, M., and Magdassi, S. (2015) 3D printing of porous structures by UV-curable O/W emulsion for fabrication of conductive objects. *J. Mater. Chem. C*, **3** (9), 2040–2044.
- 247 Salmerón, J.F., Molina-Lopez, F., Briand, D., Ruan, J.J., Rivadeneyra, A., Carvajal, M.A., Capitan-Vallvey, L.F., Derooij, N.F., and Palma, A.J. (2013) Properties and printability of inkjet and screen-printed silver patterns for RFID antennas. *J. Electron. Mater.*, **43** (2), 604–617.

- 248 Allen, M.L., Jaakkola, K., Nummila, K., and Seppa, H. (2009) Applicability of metallic nanoparticle inks in RFID applications. *IEEE Trans. Compon. Packag. Technol.*, **32** (2), 325–332.
- 249 Hu, Y., An, B., Niu, C., Lv, W. and Wu, Y. (2014) *Application of Nano Copper Conductive Ink for Printed Electronics*. Proc. 15 Inter. Conf. Electron. Packag. Technol. Aug. 12–15, 2014, TBD Chengdu, China, pp. 1565–1567.
- 250 Noguchi, Y., Sekitani, T., Yokota, T., and Someya, T. (2008) Direct inkjet printing of silver electrodes on organic semiconductors for thin-film transistors with top contact geometry. *Appl. Phys. Lett.*, **93** (4), 043303(1–3).
- 251 Whiting, G.L. and Arias, A.C. (2009) Chemically modified ink-jet printed silver electrodes for organic field-effect transistors. *Appl. Phys. Lett.*, **95** (25), 253302(1–3).
- 252 Chinga-Carrasco, G., Tobjörk, D., and Österbacka, R. (2012) Inkjet-printed silver nanoparticles on nano-engineered cellulose films for electrically conducting structures and organic transistors: Concept and challenges. *J. Nanopart. Res.*, **14** (11), 1213(1–10).
- 253 Lee, D.-H., Lim, K.-T., Park, E.-K., Kim, J.-M., and Kim, Y.-S. (2013) Optimized ink-jet printing condition for stable and reproducible performance of organic thin film transistor. *Microelectron. Eng.*, **111**, 242–246.
- 254 Takeda, Y., Yoshimura, Y., Kobayashi, Y., Kumaki, D., and Fukuda, K. (2013) Integrated circuits using fully solution-processed organic TFT devices with printed silver electrodes. *Org. Electron.*, **14** (12), 3362–3370.
- 255 Grau, G., Kitsomboonloha, R., Swisher, S.L., Kang, H., and Subramanian, V. (2014) Printed transistors on paper: Towards smart consumer product packaging. *Adv. Funct. Mater.*, **24** (32), 5067–5074.
- 256 Medina-Sánchez, M., Martínez-Domingo, X., Ramon, E., and Merkoçi, A. (2014) An ink-jet printed field-effect transistor for label-free biosensing. *Adv. Funct. Mater.*, **24** (40), 6291–6302.
- 257 Yoshimura, Y., Takeda, Y., Fukuda, K., Kumaki, D., and Tokito, S. (2014) High-speed operation in printed organic inverter circuits with short channel length. *Org. Electron.*, **15** (11), 2696–2701.
- 258 Tang, W., Feng, L., Zhao, J., Cui, Q., Chen, S., and Guo, X. (2014) Inkjet printed fine silver electrodes for all-solution-processed low-voltage organic thin film transistors. *J. Mater. Chem. C*, **2** (11), 1995–2000.
- 259 Tang, W., Feng, L., Jiang, C., Yao, G., Zhao, J., Cui, Q., and Guo, X. (2014) Controlling the surface wettability of the polymer dielectric for improved resolution of inkjet-printed electrodes and patterned channel regions in low-voltage solution-processed organic thin film transistors. *J. Mater. Chem. C*, **2** (28), 5553–5558.
- 260 Wu, Y., Li, Y., Ong, B.S., Liu, P., Gardner, S., and Chiang, B. (2005) High-performance organic thin-film transistors with solution-printed gold contacts. *Adv. Mater.*, **17** (2), 184–187.
- 261 Li, H. and Zhou, L. (2015) Effect of ambient air and temperature on ionic gel gated single-walled carbon nanotubes thin-film transistor and circuits. *ACS Appl. Mater. Interfaces*, **7** (41), 22881–22887.
- 262 Yang, Y.S., You, I.-K., Hong, S.-H., Park, J.-H., Yun, H.-G., Kang, Y.H., Lee, C., and Cho, S.Y. (2014) Influence of self-assembled monolayer on

- indium-zinc-oxide semiconductor thin-film transistors. *J. Korean Phys. Soc.*, **65** (10), 1555–1558.
- 263 Norita, S., Kumaki, D., Kobayashi, Y., Sato, T., Fukuda, K., and Tokito, S. (2015) Inkjet-printed copper electrodes using photonic sintering and their application to organic thin-film transistors. *Org. Electron.*, **25**, 131–134.
- 264 Wu, M., Gong, Z., Massoubre, D., Zhang, Y., Richardson, E., Gu, E., and Dawson, M.D. (2011) Ink-jet printed silver nanoparticle electrodes on GaN-based micro-structured light-emitting diodes. *Appl. Phys. A*, **104** (4), 1003–1009.
- 265 Kong, Y.L., Tamargo, I.A., Kim, H., Johnson, B.n., Gupta, M.K., Koh, T.-W., Chin, H.-A., Steingart, D.A., Rand, B.P., and McAlpine, M.C. (2014) 3D Printed quantum dot light-emitting diodes. *Nano Lett.*, **14** (12), 7017–7023.
- 266 Hecht, D.S., Hu, L., and Irvin, G. (2011) Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Adv. Mater.*, **23** (13), 1482–1513.
- 267 Kang, M.G., Kim, M.S., Kim, J.S., and Guo, L.J. (2008) Organic solar cell using nanoimprinted transparent metal electrodes. *Adv. Mater.*, **20** (23), 4408–4413.
- 268 Layani, M., Grouchko, M., Milo, O., Balberg, I., Azulay, D., and Magdassi, S. (2009) Transparent conductive coatings by printing coffee ring arrays obtained at room temperature. *ACS Nano*, **3** (11), 3537–3542.
- 269 Jang, Y., Kim, J., and Byun, D. (2013) Invisible metal-grid transparent electrode prepared by electrohydrodynamic (EHD) jet printing. *J. Phys. D: Appl. Phys.*, **46** (15), 155103(1–5).
- 270 Jeong, J.-A., Kim, H.-K., and Kim, J. (2014) Invisible Ag grid embedded with ITO nanoparticles layer as a transparent hybrid electrode. *Sol. Energy Mater. Sol. Cells*, **125**, 113–119.
- 271 Kahng, Y.H., Kim, M.-K., Lee, J.-H., Kim, Y.J., Kim, N., Park, D.-W., and Lee, K. (2014) Highly conductive flexible transparent electrodes fabricated by combining graphene films and inkjet-printed silver grids. *Sol. Energy Mater. Sol. Cells*, **124**, 86–91.
- 272 Jeong, J.-A., Kang, S.-B., and Kim, H.-K. (2013) Transparent Cu grid prepared by inkjet printing with Cu nanoparticle ink. *J. Korean Phys. Soc.*, **63** (1), 62–66.
- 273 He, W. and Ye, C. (2015) Flexible transparent conductive films on the basis of Ag nanowires: Design and applications: A review. *J. Mater. Sci. Technol.*, **31** (6), 581–588.
- 274 Sun, Y. (2010) Silver nanowires – unique templates for functional nanostructures. *Nanoscale*, **2** (9), 1626–1642.
- 275 Komoda, N., Nogi, M., Suganuma, K., Kohno, K., Akiyama, Y., and Otsuka, K. (2012) Printed silver nanowire antennas with low signal loss at high-frequency radio. *Nanoscale*, **4** (10), 3148–3153.
- 276 Wu, J.-T., Hsu, S.L.-C., Tsai, M.-H., Liu, Y.-F., and Hwang, W.-S. (2012) Direct ink-jet printing of silver nitrate–silver nanowire hybrid inks to fabricate silver conductive lines. *J. Mater. Chem.*, **22** (31), 15599–15605.

- 277 Lu, H., Lin, J., Wu, N., Nie, S., Luo, Q., Ma, C.-Q., and Cui, Z. (2015) Inkjet printed silver nanowires network as top electrode for semi-transparent organic photovoltaic devices. *Appl. Phys. Lett.*, **106** (9), 093302(1–4).
- 278 Finn, D.J., Lotya, M., and Coleman, J.N. (2015) Inkjet printing of silver nanowires networks. *ACS Appl. Mater. Interfaces*, **7** (17), 9254–9261.
- 279 Neophytou, M., Hermerschmidt, F., Savva, A., Georgiou, E., and Choulis, S.A. (2012) Highly efficient indium tin oxide-free organic photovoltaics using inkjet-printed silver nanoparticle current collective grids. *Appl. Phys. Lett.*, **101** (19), 193302(1–4).
- 280 Sun, Y., Zhang, Y., Liang, Q., Zhang, Y., Chi, H., Shi, Y., and Fang, D. (2013) Solvent inkjet printing process for the fabrication of polymer solar cells. *RSC Adv.*, **3** (30), 11925–11934.
- 281 Hösel, M., Søndergaard, R.R., Angmo, D., and Krebs, F.C. (2013) Comparison of fast roll-to-roll flexographic, inkjet, flatbed, and rotary screen printing of metal black electrodes for polymer solar cells. *Adv. Eng. Mater.*, **15** (10), 995–1001.
- 282 Angmo, D., Larsen-Olsen, T.T., Jørgensen, M., Søndergaard, R.R., and Krebs, F.C. (2013) Roll-to-roll inkjet printing and photonic sintering of electrodes for ITO free polymer solar cell modules and facile product integration. *Adv. Energy Mater.*, **3** (2), 172–175.
- 283 Galagan, Y., Coenen, E.W.C., Abbel, R., van Lammeren, T.J., Sabik, S., Barink, M., Meinders, E.R., Andriessen, R., and Blom, P.W.M. (2013) Photonic sintering of inkjet printed current collecting grids for organic solar cell applications. *Org. Electron.*, **14** (1), 38–46.
- 284 Van Freneker, J.J., Voorthuijzen, W.P., Gorter, H., Hendriks, K.H., Janssen, R.A.J., Hadipour, A., Andriessen, R., and Galagan, Y. (2013) All-solution-processed organic solar cells with conventional architecture. *Sol. Energy Mater. Sol. Cells*, **117**, 267–272.
- 285 Angmo, D., Sweelssen, J., Andriessen, R., Galagan, Y., and Krebs, F.C. (2013) Inkjet printing of back electrodes for inverted polymer solar cells. *Adv. Energy Mater.*, **3** (9), 1230–1237.
- 286 Neophytou, M., Georgiou, E., Fyrillas, M.M., and Choulis, S.A. (2014) Two step sintering process and metal grid design optimization for highly efficient ITO free organic photovoltaics. *Sol. Energy Mater. Sol. Cells*, **122**, 1–7.
- 287 Burgués-Ceballos, I., Kehagias, N., Sotomayor-Torres, C.M., Campoy-Quiles, M., and Lacharmoise, P.D. (2014) Embedded inkjet printed silver grids for ITO-free organic solar cells with high fill factor. *Sol. Energy Mater. Sol. Cells*, **127**, 50–57.
- 288 Galagan, Y., Shanmugan, S., Teunissen, J.P., Eggenhuisen, T.M., Biezemans, A.F.K.V., Van Gijsegheem, T., Groen, W.A., and Andriessen, R. (2014) Solution processing of back electrodes for organic solar cells with inverted architecture. *Sol. Energy Mater. Sol. Cells*, **130**, 163–169.
- 289 Jung, S., Sou, A., Banger, K., Ko, D.-H., Chow, P.C.Y., McNeill, C.R., and Sirringhaus, H. (2014) All-inkjet-printed, all-air-processed solar cells. *Adv. Energy Mater.*, **4** (14), 1400432(1–9).

- 290 Hu, B.-C., Weng, R.-H., and Chen, C.-T. (2014) Silver conducting lines of dye-sensitized solar cells printed onto commercial building tiles. *Procedia Eng.*, **79**, 267–272.
- 291 Murali, B., Kim, D.-G., Kang, J.-W., and Kim, J. (2014) Inkjet printing of hybrid transparent conducting electrodes for organic solar cells. *Phys. Status Solidi A*, **211** (8), 1801–1806.
- 292 Eggenhuisen, T.M., Galagan, Y., Biezemans, A.F.K.V., Staats, T.M.W.L., Voorthuijzen, W.P., Kommeren, S., Shanmugan, S., Teunissen, J.P., Hadipour, A., Verhees, W.J.H., Veenstra, S.C., Coenen, M.J.J., Gilot, J., Andriessen, R., and Groen, W.A. (2015) High efficiency, fully inkjet printed organic solar cells with freedom of design. *J. Mater. Chem. A*, **3** (14), 7255–7262.
- 293 Patil, B.R., Shanmugan, S., Teunissen, J.-P., and Galagan, Y. (2015) All-solution processed organic solar cells with top illumination. *Org. Electron.*, **21**, 40–46.

8

Graphene- and 2D Material-Based Thin-Film Printing

Jiantong Li, Max C. Lemme, and Mikael Östling

8.1 Introduction

Printing is a process to reproduce patterns such as text and images. It played an important role in the development of the Renaissance and scientific revolution and laid the material basis for the modern knowledge-based economy and the spread of learning to the masses [1]. Recently, the traditional printing techniques have been applied in the emerging field – printed electronics. Through integration with functional electronic materials, such as metal nanoparticles, conducting polymer, carbon nanotubes, graphene, and other 2D materials, printing techniques are employed to fabricate various intelligent components and smart systems for emerging electronics, including organic light-emitting diodes, displays, thin-film transistors, memories, batteries, and microelectromechanical systems [2–4]. Depending on the applications, the devices/components are printed on various substrates, such as silicon wafers, glass, plastics, and paper. The key to most applications is to print reliably and efficiently thin films of the electronic materials in predefined patterns and locations. Among the various printing techniques, inkjet printing receives great interest in the field of printed electronics. It prints patterns by ejecting ink droplets through nozzles onto substrates. In principle, it enables direct writing of patterned thin films of versatile materials (in the inks) at any arbitrary location on almost all kinds of substrates. This merit is attractive for emerging electronics where the devices are desired to be fabricated onto a certain substrate and directly integrated with other components. Inkjet printing is anticipated to play a more and more important role in printed electronics.

Meanwhile, the family of 2D materials, such as graphene and MoS_2 , has been attracting great attention in various research fields, including electronics, energy storage, sensing, and biology [5]. Their unique structure, single or few layers of atoms, enables the integration of a number of excellent properties. For instance, graphene (a layer of carbon atoms) is electrically and thermally conductive, optically transparent, and mechanically flexible. Besides, 2D materials typically possess extremely high specific surface area (e.g., the theoretical value of graphene is $2630 \text{ m}^2 \text{ g}^{-1}$), a fascinating merit for energy storage applications. Furthermore, most 2D materials are compatible with liquid-phase fabrication. A variety of techniques have been developed to prepare liquid dispersions of the 2D materials,

such as sonication-assisted exfoliation [6], electrochemical exfoliation [7], shear exfoliation [8], and chemical exfoliation (lithium intercalation) [9]. These techniques pave the way for the combination between the unique 2D materials and the promising inkjet printing technique to generate innovative applications [5, 10].

In this chapter, we mainly review the status of inkjet printing techniques of 2D material for thin-film fabrication. Despite a number of studies on thin-film printing of 2D materials in the literature, here we mainly include those that produce films with high resolution, high uniformity, and high performance, and/or with innovative applications. In the following sections, the procedures of inkjet printing of 2D materials (Section 8.2) are first introduced, followed by the discussion about the performance and applications of printed 2D materials (Section 8.3). This chapter ends with the summary of the present status and outlook for the future trend in the fields (Section 8.4).

8.2 Printing Procedures

In printed electronics, inkjet printing of functional nanomaterials typically comprises four processes: ink formulation, printing (jetting of inks to form patterns), ink drying (solvent evaporation), and posttreatments (sintering or annealing). Each process plays a role in fabricating high-quality patterns or thin films. With respect to inkjet printing of 2D materials, special attention should be paid to the processes, as detailed in the following sections.

8.2.1 Ink Formulations

Stable inks with compatible rheology and particle size are a prerequisite for inkjet printing. Two types of inks are generally used for inkjet printing of graphene and 2D materials [11]. One is binder-free inks where the raw materials (graphite or bulk layered materials) are directly exfoliated (with the assistance of sonication or shear [12]) in organic solvents, such as *N*-methyl-2-pyrrolidone (NMP) [13] and dimethylformamide (DMF), followed by centrifugation at certain rate (usually around 5000 rpm) to remove the big particles. In order to avoid severe nozzle clogging, the lateral dimension of 2D materials in the inks should be less than 1/20 of the nozzle diameter. A solvent is predicted to disperse well a 2D material if it has adaptable Hansen solubility parameters (dispersive, polar, and H-bonding components of the cohesive energy density) to the latter [6, 14]. Based on this prediction, it has been found that some solvent mixtures can also disperse well 2D materials, even though each individual solvent does poorly [14]. For example, with certain composition, the ethanol/water mixture effectively disperses MoS₂, WS₂, and BN, and the water/isopropanol or water/ethanol mixture disperses graphene well [15]. Binder-free graphene inks with either single solvents or mixed solvents have been used for inkjet printing [13, 16]. One important advantage of binder-free inks is that no high-temperature annealing is needed to obtain good conductivity. Finn *et al.* [17] demonstrated a conductivity of about 3000 S m⁻¹ for the printed graphene films (with NMP-based inks) after annealing only at 70 °C. However, there are also evident shortcomings for

binder-free inks. First, the ink solvents do not possess preferable rheology for inkjet printing. Inkjet printing favors a viscosity of about 10 cP at operating temperature, whereas the common solvents for 2D materials dispersions (NMP, DMF, as well as water/alcohol mixtures) have viscosity less than 2 cP. It may reduce the controllability during the course of jetting and thereby make it challenging to produce high-resolution patterns. As a matter of fact, few studies have demonstrated printed patterns with well-defined dimension less than 1 mm, which severely restricts the applications in printed electronics where the feature size is typically at the level of 100 μm . Second, without binders, the 2D materials in the ink tend to aggregate, which may clog the nozzles and diminish the jetting reliability. Third, many organic solvents for binder-free 2D material inks are toxic. These factors might hamper the upscaling of binder-free inks for printed electronics.

The other type is binder-containing inks. In these inks, binders are used to prevent the sedimentation of the 2D materials and can greatly improve the printing quality and reliability. The shortcoming of binder-containing inks is that after printing, high-temperature ($\sim 400^\circ\text{C}$) annealing is typically needed to get rid of the binders and attain conductive films, which is incompatible with most flexible substrates, such as paper and plastics. The widely used binders for 2D material inks include ethyl cellulose (EC) [18–22] and polyvinylpyrrolidone (PVP) [23]. Among them, EC is the most popular one because it can significantly extend the stable period of the ink at high load ($>1\text{ mg ml}^{-1}$) of 2D materials [12, 18–22], can increase the uniformity of printed patterning during ink drying [24], and can be readily removed by annealing at a relatively low temperature of $300\text{--}400^\circ\text{C}$ [18]. A striking significance of binder-containing inks is that the solvents are not restricted to those with adaptable Hansen solubility parameters to 2D materials. This thereby offers opportunities to use environmentally friendly and inkjet-compatible solvents to formulate 2D material inks. One of such promising solvents is terpineol. It is much less toxic than NMP or DMP and has a high viscosity of about 40 cP, which, after being tailored by ethanol [20] or cyclohexanone [18], is very attractive for inkjet printing as well as other printing techniques (e.g., screen printing). In particular, the graphene/terpineol/EC ink system often exhibits a stable period over several months and has been used by several groups to reliably print patterns at a resolution of about 50 μm [18, 19].

However, there is no demonstration for the direct formulation of the graphene/terpineol/EC inks. A possible reason is that graphite cannot be directly exfoliated in terpineol. In practice, the strategy of solvent exchange is adopted to formulate the graphene/terpineol/EC inks. The principle is that graphene (or other 2D materials) is first exfoliated in one solvent (exfoliation solvent) and protected by stabilizing polymers, and then the exfoliation solvent is exchanged with another solvent (printing solvent) that is of low toxicity and compatible with inkjet printing. At least two kinds of implementations have been demonstrated. Secor *et al.* [18] exfoliated graphene in ethanol in the presence of EC (Figure 8.1a), followed by centrifugation to remove large graphite particles (Figure 8.1b), and then aqueous NaCl solution is added to flocculate graphene/EC composite (Figure 8.1c). Finally, the harvested graphene/EC

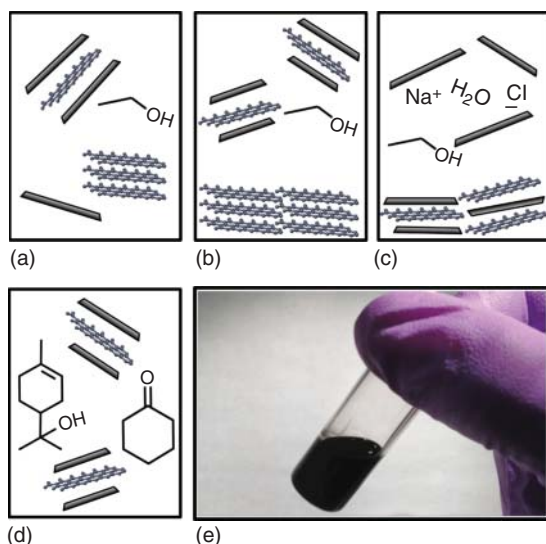


Figure 8.1 Schematic illustration of the ink preparation method. (a) Graphene is exfoliated from graphite powder in ethanol/EC. (b) The graphene/EC/ethanol dispersion is centrifuged to remove large graphite flakes. (c) Graphene/EC powder is obtained from salt-induced flocculation. (d) The final ink is prepared by the dispersion of graphene/EC powder in the ratio of 85 : 15 cyclohexanone/terpineol. (e) Vial of the prepared graphene ink. (Secor *et al.* (2013) [18]. Reproduced with permission of American Chemical Society.)

composite is dispersed in a mixture of cyclohexanone/terpineol (Figure 8.1d) to obtain the graphene inks (Figure 8.1e). In these inks, the graphene flakes are typically 2 nm thick, with a lateral dimension of about 50 nm.

Li *et al.* developed a simple and scalable distillation-assisted solvent exchange technique [25] to formulate high-quality inkjet printing inks of 2D materials [19–21], as illustrated in Figure 8.2. First, graphene or other 2D nanosheets are directly exfoliated in DMF, followed by a high-rate centrifugation to sediment the large particles. Later, EC and terpineol are added as the stabilizing polymer and printing solvent, respectively. Finally, DMF is distilled off, and both graphene and EC are transferred to terpineol. After the rheology is tailored by ethanol, the inks are ready for inkjet printing. The solvent exchange technique uses the difference in boiling points of DMF (boiling point 153 °C) and terpineol (boiling point ~220 °C). For the practical distillation, a rotary evaporation is used so that DMF can be distilled off at a low temperature (80 °C) under a reduced pressure of ~30 mbar. During distillation, terpineol has much lower volume than DMF (DMF:terpineol volume ratio is up to 60:1) so that the final graphene ink is greatly concentrated. The graphene in the inks are mostly of five flake layers with the lateral dimension ranging between 100 and 500 nm.

Several advantages are clear for the distillation-assisted solvent exchange technique: (i) the technique distinctly separates the exfoliation process and solvent exchange process. Thereby, it can be readily generalized to all other 2D materials as long as they can be exfoliated in certain solvents. (ii) The technique is fairly simple in that only one distillation process accomplishes the solvent exchange. (iii) Throughout the solvent exchange process, the 2D materials retain in liquid phase, which to the largest extent prevents the restacking of 2D material flakes. (iv) Almost all 2D material flakes are finally transferred into the printable solvents, greatly reducing material waste. (v) In spite of the preference of low-boiling-point solvents in many other applications, inkjet printing usually

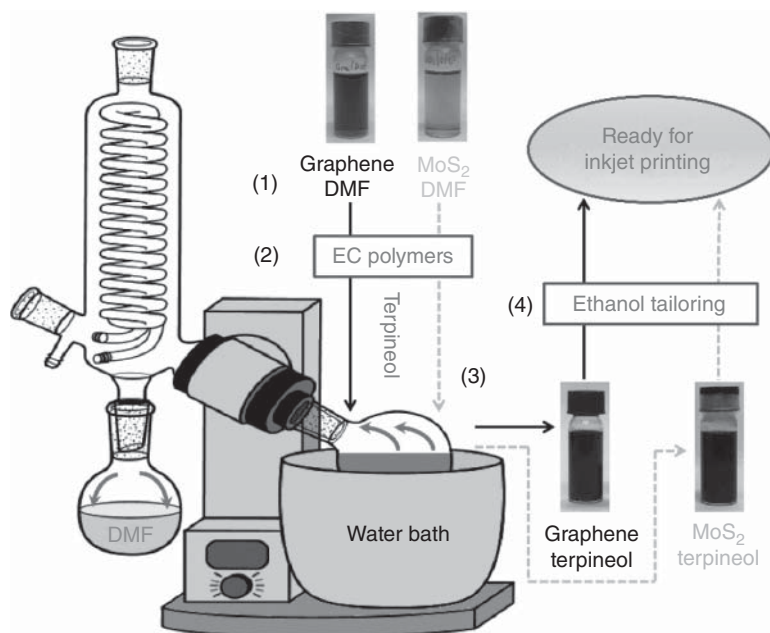


Figure 8.2 Schematic illustration of the ink formulation concept for inkjet printing of 2D-layered materials based on the distillation-assisted solvent exchange technique. (Li *et al.* (2014) [20]. Reproduced with permission of Wiley.)

favors high-boiling-point inks since volatile inks dry quickly and hence easily clog the nozzles. Therefore, the distillation-assisted solvent exchange technique ideally suits inkjet printing.

Recently, Majee *et al.* [12] formulated another kind of binder-containing graphene ink without using solvent exchange process. Graphene is dispersed in NMP through shear exfoliation. After big particles are sedimented through centrifugation, EC and ethylene glycol are added to stabilize graphene and tailor the ink viscosity, respectively. Because of the presence of NMP, only a small amount of EC is needed to stabilize the ink. As a result, the printed graphene films are conductive without any high-temperature annealing, although the annealing can further improve the conductivity. The graphene flake is mostly around 2 nm thick with a lateral dimension of about 160 nm. The graphene concentration is over 3 mg ml⁻¹. This technique makes trade-off between binder-free inks and typical binder-containing inks and is expected to extend the applications of graphene inks as long as the issue of solvent toxicity can be addressed.

Dodoo-Arhin *et al.* [23] used PVP as a special binder to formulate graphene inks. PVP has a structure that is analogous to NMP and can stabilize graphene for a long time. The ink is formulated very simply by mixing PVP and graphite at the mass ratio of about 1 : 100 in isopropanol and sonicating at 15 °C for 12 h. Later, centrifugation and vacuum filtration are used to remove big particles. The obtained graphene inks can be stable for several months. Most of the graphene flakes are about 4 nm thick and 200 nm wide. In this formulation, PVP has dual

Table 8.1 Properties of 2D materials in different inks.

Ink composition	Flake size (nm)	Flake thickness or layer number	Concentration (mg ml ⁻¹)	Reference
Graphene/NMP	173	4 layers	6	Finn <i>et al.</i> [17]
Graphene/ethanol/H ₂ O	<2000		0.6	Capasso <i>et al.</i> [16]
Graphene/EC/cyclohexanone/terpineol	50	2 nm	3	Secor <i>et al.</i> [18]
Graphene/EC/terpineol/ethanol	100–500	5 layers	1	Li <i>et al.</i> [19]
MoS ₂ /EC/terpineol/ethanol	40–100	5–7 nm	0.1	Li <i>et al.</i> [21]
Graphene/EC/NMP/ethylene glycol	160	2 nm	3	Majee <i>et al.</i> [12]
Graphene/PVP/isopropanol	200	4 nm		Dodoo-Arhin <i>et al.</i> [23]

functions. One is to exfoliate graphite to graphene and extend the stable period of the ink. The other is to tailor the ink rheology to be compatible with inkjet printing.

For clear comparison, the aforementioned techniques are briefly summarized in Table 8.1.

8.2.2 Jetting and Patterns

Once the 2D material inks have proper rheology (viscosity around 10 cP and surface tension around 30 mN m⁻¹ at operating temperature), small particle size (less than 1/20 of nozzle diameter), and sufficiently long stable period, they can be well jetted out of inkjet printers. The widely used inkjet printer in the literature is the commercially available FujiFilm Dimatix Material Printer. With proper parameter settings (driving voltage and waveform, jetting temperature, firing frequency, etc.), we have demonstrated [19, 21] excellent jetting performance for our graphene and MoS₂ inks, as shown in Figure 8.3 where the ink droplets are well directed and constantly jetted out of all nozzles at an even velocity. The reliable jetting enables parallel printing with multiple nozzles to allow efficient large-scale production. Figure 8.4 shows the printed patterns (droplet matrix, lines, and films for graphene and MoS₂). In particular, the printed lines are smooth, even, narrow, and straight. These are indispensable features for future applications in printed electronics [26, 27]. In principle, the reliable printing allows efficient printing of any patterns at a resolution of about 50 μm, even including complicated patterns. For example, in Figure 8.5, the KTH logo is printed with the graphene inks and conforms well to the design.

8.2.3 Drying

A general phenomenon during the drying of liquid drops is the “coffee-ring” effect [28]. When a liquid drop dries, the contact line is typically pinned because of the rough structure or chemical heterogeneity on the surface or because of the solutes

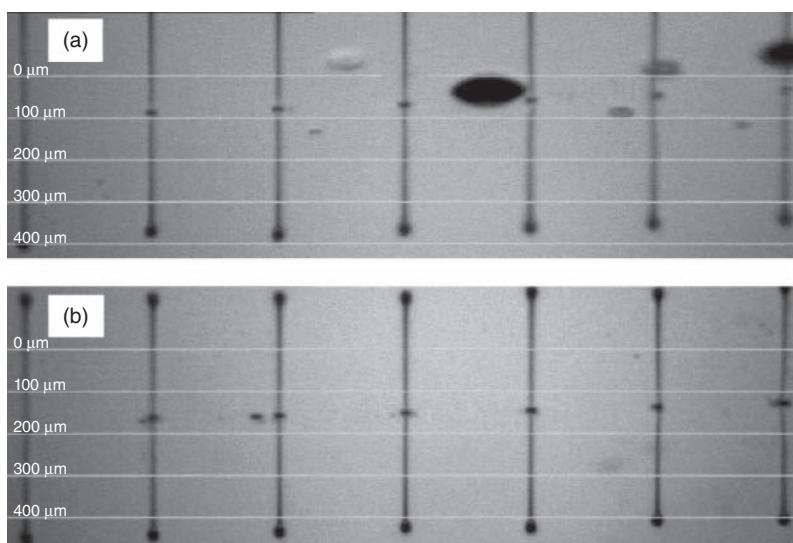


Figure 8.3 Stroboscopic images of jetted droplets showing the jetting performance of (a) graphene (Li *et al.* (2013) [19]. Reproduced with permission of Wiley) and (b) MoS₂ inks (Li *et al.* (2014) [21]. Reproduced with permission of Wiley.)

deposited on the substrate [26]. Then, the liquid at the edge evaporates faster and is then replenished by the liquid from the interior [28]. The outward flow carries the solute to the boundary, resulting in “ring-like” films (boundary is thicker than the interior). Since the coffee-ring effect gives rise to nonuniform patterns, it is usually undesired for thin-film printing. There are several strategies to suppress the coffee-ring effect, including depinning the contact lines, using anisotropic particles, introducing the inward Marangoni flow, and adjusting substrate temperature during drying [26].

Since contact line pinning is a prerequisite for the coffee-ring effect, depinning contact line can effectively avoid the effects. To implement this idea, Song *et al.* [26, 29] modified the substrates with high receding contact angle to allow the free sliding of contact line. They have demonstrated that ring-like morphology forms on substrate with low contact angle due to the pinned contact line while it is suppressed on high contact angle (Figure 8.6a).

Using appropriate particle shape is another way to eliminate the coffee-ring effect. Yunker *et al.* [30] demonstrated experimentally that ellipsoidal particles are deposited uniformly. The anisotropic shape of the particles can significantly deform air–water interfaces and produce strong interparticle capillary interactions. Thus, when the ellipsoids are carried to the air–water interface by the outward flow, the strong long-ranged interparticle attractions between ellipsoids lead to the formation of loosely packed or arrested structures on the air–water interface. These structures prevent the suspended particles from reaching the drop edge and give rise to uniform deposition (Figure 8.6b). In particular, under appropriate conditions, suspensions of spheres mixed with just a small number of ellipsoids also produce uniform deposition.

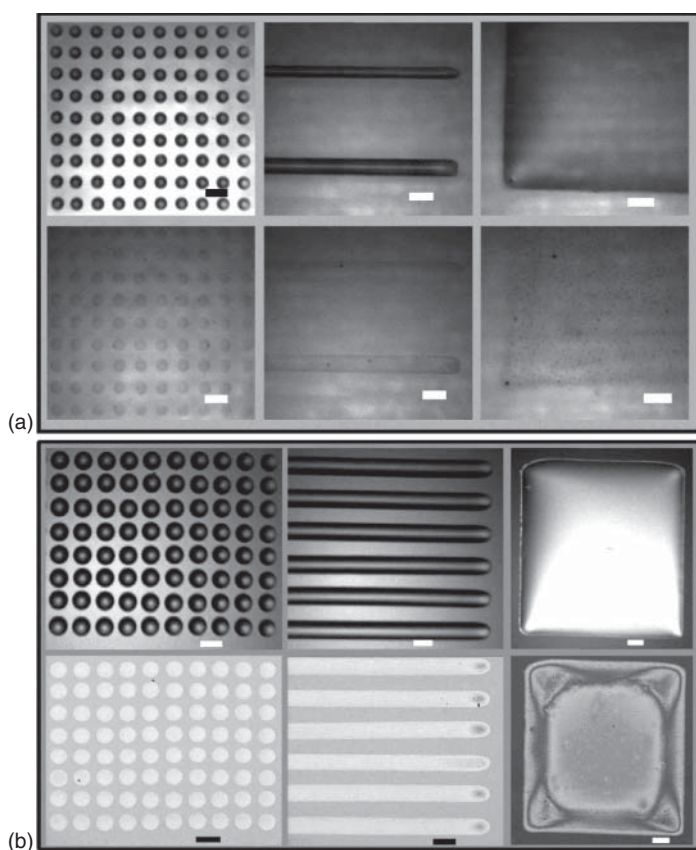


Figure 8.4 As-printed (upper) and dried (lower) patterns for inkjet printing of (a) graphene (Li *et al.* (2013) [19]. Reproduced with permission of Wiley) and (b) MoS₂ (Li *et al.* (2014) [21]. Reproduced with permission of Wiley). Scale bars: 100 μ m.

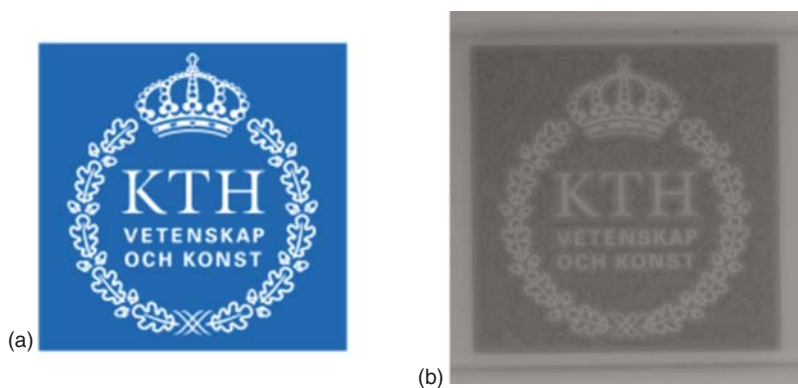


Figure 8.5 Inkjet-printed KTH logo on glass slides (b) with graphene inks [19]. (a) The original design.

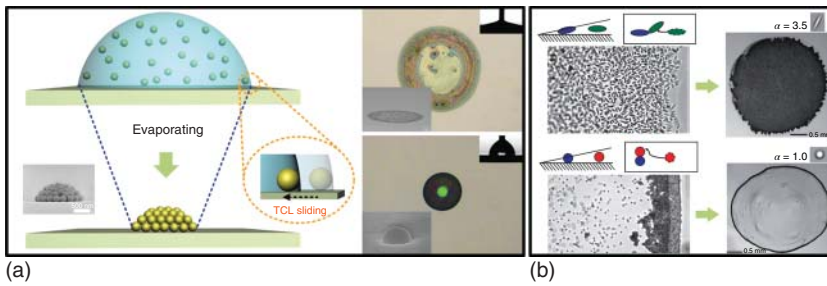


Figure 8.6 (a) Left: illustration for the sliding of contact lines to suppress coffee-ring effects. Right: optical images and SEM images (insets) of printed dots on substrate with low contact angle (upper) and high contact angle (lower). (Reproduced with permission from [26, 29].) (b) Optical images of the packing structure (left) and the corresponding final deposition morphology (right) of ellipsoidal particles and spherical particles. (Reproduced with permission from [26, 30].)

A third strategy is to introduce the inward Marangoni flow to balance the outward flow during evaporation and attain uniform deposition. Marangoni flow is generated by surface tension gradient where the fluid flows from the low-surface-tension region to the high-surface-tension region. A practical way is to add a solvent of higher boiling point and lower surface tension into the inks. When the drop dries, the added solvent evaporates slowly in the boundary, which thereby has lower surface tension. Then, the inward Marangoni flow forms from the boundary (low-surface-tension region) to the center (high-surface-tension region). In this way, the outward flow is compensated and the coffee-ring effects are suppressed [31].

Finally, Soltman and Subramanian [27] demonstrated that the substrate temperature also plays an important role in the ink drying. A heated substrate leads to greater evaporation at the edge and enhances the coffee-ring effect, whereas a cooled substrate suppresses the evaporation at the edge and eliminates the coffee-ring effect.

As for inkjet printing of 2D materials, some studies [18, 19] have also demonstrated the suppression of coffee-ring effects through different strategies. Li *et al.* [19] printed the graphene inks with mixed solvents, terpineol and ethanol, and observed the depinning of the contact lines during ink drying. Before drying, the binary-solvent inks wet well on a substrate (Figure 8.7a). During drying, ethanol evaporates faster and the remaining terpineol has poor wetting on the substrate (or some deposited graphene/EC film), which depins the contact lines and suppresses the coffee-ring effect (Figure 8.7b). However, the dewetting of terpineol also causes nonuniformity in the patterns. To overcome this issue, the substrate is heated up to alleviate the dewetting and quickly reach uniform patterns (Figure 8.7c). As a result, highly uniform patterns can be obtained, as shown in Figure 8.8, where the atomic force microscopy analyses indicate that the printed droplet and line are free from coffee-ring effects. However, it is worth mentioning that the contact line depinning strongly depends on the materials in the inks. During the drying of MoS_2 inks with identical composition, the pinning of contact lines is still observed (Figure 8.4b) [21].

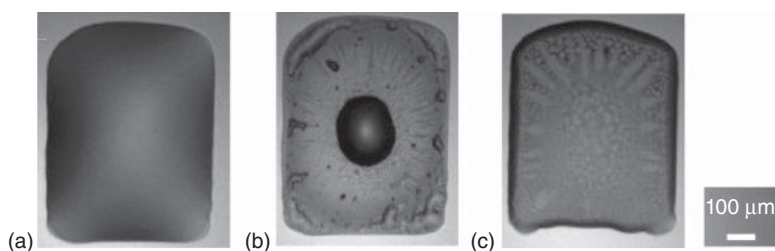


Figure 8.7 Evaporation processes of inkjet-printed graphene films on silicon. (a) Optical micrograph of an as-printed liquid film. (b) The dried pattern with the substrate at room temperature. The dark region in the center consists of the dewetted terpeneol. (c) The dried pattern with the substrate at 60 °C. There is no dewetting and the pattern is fairly uniform. (Li *et al.* (2013) [19]. Reproduced with permission of Wiley.)

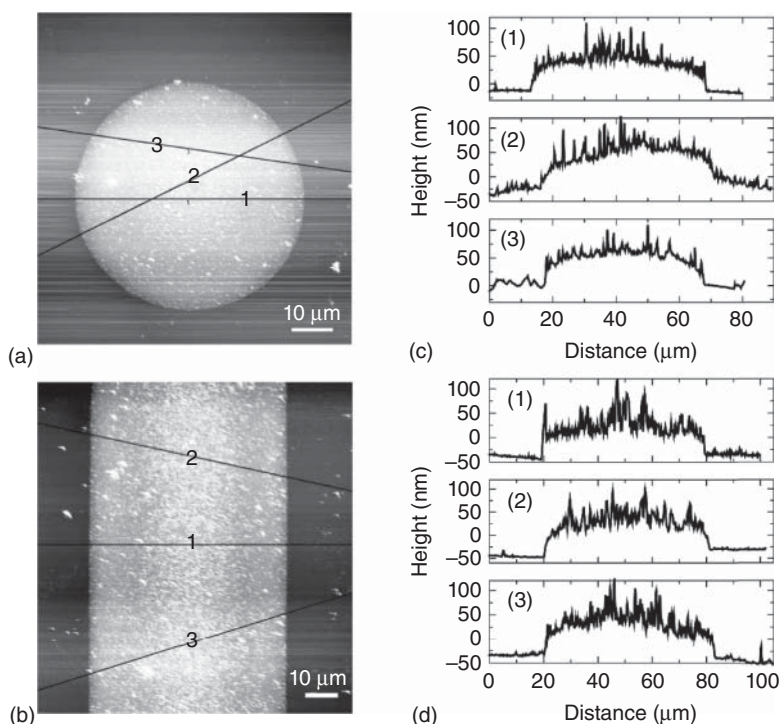


Figure 8.8 AFM images of a dried droplet (a) and line (b) printed for the printed graphene patterns in Figure 8.4a. (c, d) Cross-sectional profiles along the three directions in (a) and (b), respectively. The patterns are globally uniform (free from the coffee-ring effect). (Li *et al.* (2013) [19]. Reproduced with permission of Wiley.)

In addition, Secor *et al.* [18] demonstrated that during drying, the graphene inks with mixed solvents, cyclohexanone and terpeneol, are also free from coffee-ring effects (Figure 8.9). It was ascribed to the introduction of inward Marangoni flow. Compared with cyclohexanone (boiling point: 156 °C, surface tension: 34.4 mN m⁻¹), terpeneol (boiling point: 218 °C, surface tension:

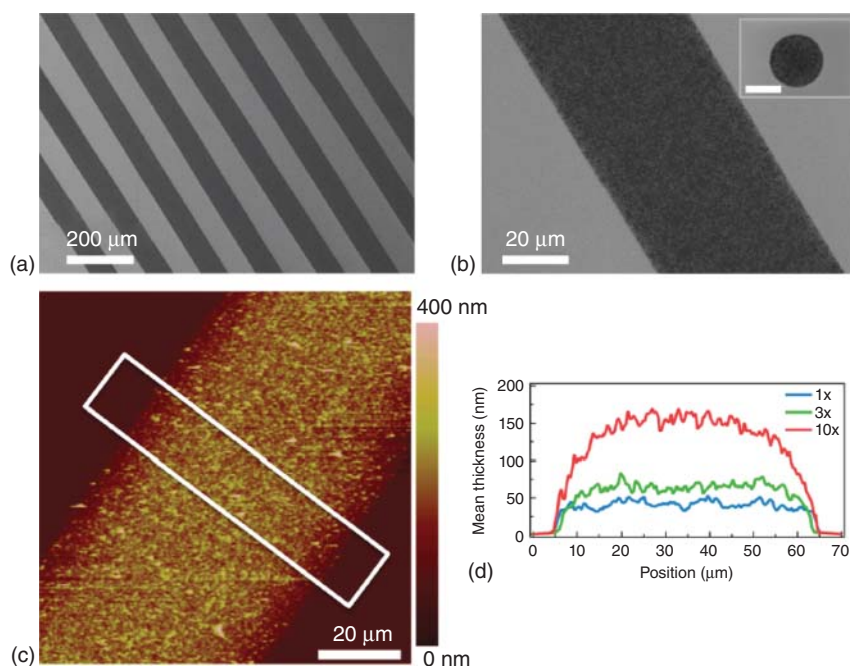


Figure 8.9 Morphology of inkjet-printed graphene features on HMDS-treated Si/SiO₂ wafer illustrating the uniformity of the printed features. SEM images of (a) multiple printed lines and (b) a single printed line and drop (inset: scale bar corresponds to 40 μm). (c) AFM image of a single line following 10 printing passes and (d) averaged cross-sectional profiles (over the boxed region in (c)) of printed lines after 1, 3, and 10 printing passes, demonstrating the uniform patterns free from coffee-ring effects even after multiple printing passes. (Secor *et al.* (2013) [18]. Reproduced with permission of American Chemical Society.)

33.2 mN m⁻¹) has higher boiling point and slightly lower surface tension, which is feasible to form the inward Marangoni flow.

For most applications of printed graphene and 2D materials, it is of crucial importance to suppress the coffee-ring effect and print uniform thin films. The aforementioned four strategies are valuable for practical ink formulation. But one should note that the strategies are case dependent and sometimes more than one strategy should be implemented synergistically to attain uniform films.

8.2.4 Posttreatments

After ink drying, the printed 2D material thin films are often insulating (for binder-containing inks) or less conductive (for binder-free inks). They need to be annealed during the posttreatments to obtain the desired performance, especially for films printed with binder-containing inks where the binders must be removed. When EC or PVP is the binder, a simple thermal annealing ranging from 250 to 400 °C is effective to remove the binder and attain conductive films, although the optimal annealing temperature may vary with the ink composition and formulation [12, 18, 19].

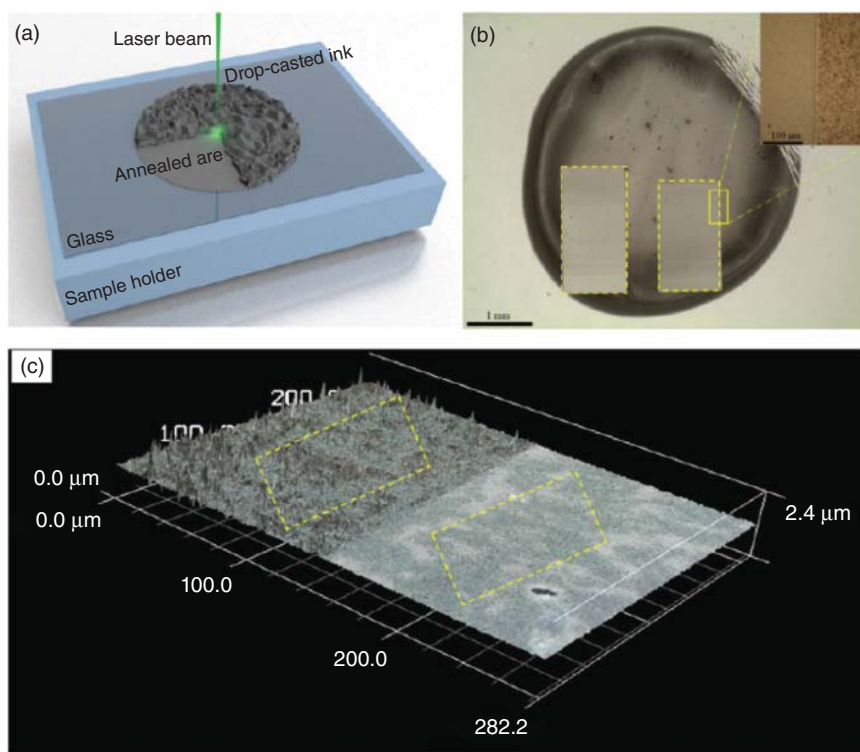


Figure 8.10 (a) Schematic illustration of the laser annealing process for films made from graphene inks. (b) Optical microscope image of a drop-cast graphene film where the laser-treated areas are marked by dotted rectangle (inset: close-up view of the border area). (c) 3D image of the surface topography by laser scanning microscope indicating the difference between the areas with and without laser annealing. (Del *et al.* (2015) <http://iopscience.iop.org/article/10.1088/2053-1583/2/1/011003/meta>. Used under CC BY 3.0 <https://creativecommons.org/licenses/by/3.0/>.)

For thin films printed with binder-containing inks, a rough surface with many standing-up graphene flakes is typically obtained. The rough surface is attractive for some applications, such as supercapacitors and sensors. But many other applications may require smooth surface, such as transparent conductors. In order to further improve the morphology and optimize the performance of printed graphene films, Del *et al.* [32] recently developed an effective laser annealing technique. The main function of the laser annealing is to flatten the standing-up graphene flakes and hence smoothen the film surface (Figure 8.10). As a result, both transmittance and conductance of the graphene films can be improved considerably [32].

8.3 Performance and Applications

In this section, we introduce several electronic applications based on inkjet-printed 2D material thin films in the literature, including transparent conductors, micro-supercapacitors, photodetectors, and solar cells.

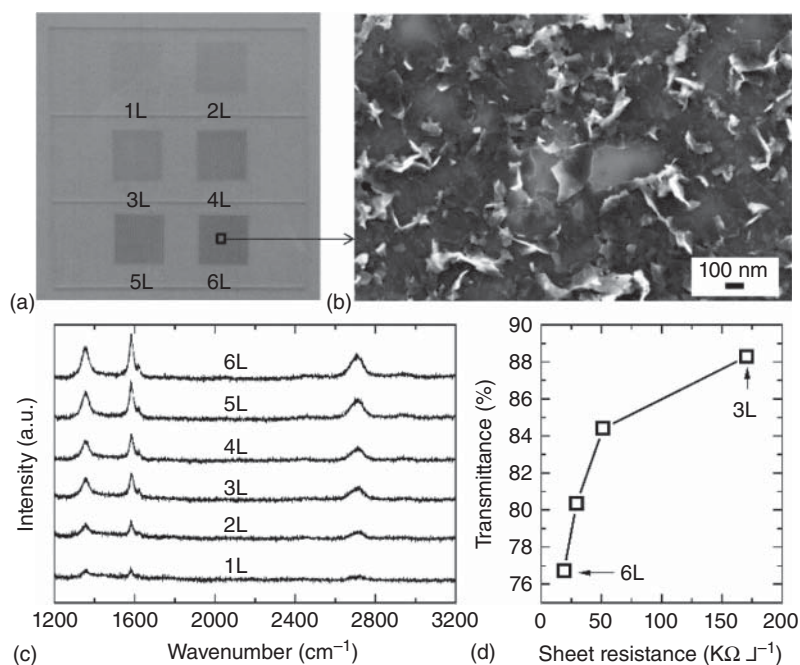


Figure 8.11 Printed graphene transparent conductive films on glass. (a) Printed graphene square films ($1.5\text{ cm} \times 1.5\text{ cm}$) with various printing layers (from 1–6 layers). (b) An SEM image of the six-layer (6L) graphene film. (c) Raman spectra of the printed graphene films. (d) Transmittance (at the wavelength of 550 nm) versus sheet resistance for some printed graphene films (3–6 printing layers). (Li *et al.* (2013) [19]. Reproduced with permission of Wiley.)

8.3.1 Transparent Conductors

Because graphene is both electrically conductive and optically transparent, a promising application of the printed graphene films is transparent conductors. Compared with other fabrication techniques, inkjet printing can readily tailor the film transmittance and sheet resistance adjusting the number of printing passes. Figure 8.11 indicates one example of the printed graphene square films and the relationship between their transmittance and sheet resistance [19]. Table 8.2 summarizes the device performance of printed graphene transparent conductors in the literature.

8.3.2 Micro-Supercapacitors

As a relatively new type of energy storage devices, supercapacitors have received great research interest. Because of the good electrical conductivity, high specific surface area, and electrochemical stability, graphene has been demonstrated as ideal electrode materials for supercapacitor applications [33]. The present trend toward miniaturized portable electronic devices has increased the demand for compact energy storage devices, which can be integrated directly with other electronic components. Planar micro-supercapacitors (mSCs) [34] are promising devices for such applications. In comparison with the stacked structure

Table 8.2 Performance of inkjet-printed graphene-based transparent conductors.

Ink composition	Sheet resistance ($\text{k}\Omega \square^{-1}$)	Transmittance (%)	Post-treatment ($^{\circ}\text{C}$)	Reference
Graphene/NMP	100	70	170	Torrise <i>et al.</i> [13]
Graphene/ethanol/ H_2O	80	55	No	Capasso <i>et al.</i> [16]
Graphene/EC/terpineol/ethanol	50	84	400	Li <i>et al.</i> [19]
Graphene/EC/NMP/ethylene glycol	0.8	66	No	Majee <i>et al.</i> [12]
Graphene/EC/NMP/ethylene glycol	0.3	86	350	Majee <i>et al.</i> [12]
Graphene/cyclohexanone	0.8	60	300	Gao <i>et al.</i> [22]

of conventional supercapacitors, mSCs have planar (usually interdigitated) structure, which greatly simplifies the device fabrication and system integration. However, patterning on an arbitrary substrate is indispensable in order to fabricate such planar mSCs. Inkjet printing of graphene provides an effective solution to this application. Figure 8.12 shows the inkjet-printed mSCs on Kapton [19, 20]. The current collectors are printed with commercial silver nanoparticle inks, and the electrodes are printed with the graphene inks. With only eight printing passes of graphene, the mSCs achieve a capacitance of 0.6 mF cm^{-2} at a scan rate of 100 mV s^{-1} , comparable to similar mSCs made from laser scribing technique [35]. In addition, the devices exhibit low equivalent series resistance ($\sim 8.7 \Omega$) and rapid frequency response (the resistance–capacitance time constant is 13 ms, compared with a typical value of 1 s for normal commercial supercapacitors). The direct patterning merit of inkjet printing facilitates the fabrication of asymmetric mSCs (Figure 8.12c) where only one set of fingers are covered by printed graphene. These suggest that inkjet-printed graphene thin films will have promising applications in mSCs.

8.3.3 Photodetectors

Many 2D materials, including graphene and MoS_2 , are promising candidate materials for photodetectors [36, 37]. Photodetectors based on printed MoS_2 have also been demonstrated in the literature. Li *et al.* [21] printed MoS_2 photodetectors on SiO_2/Si substrates. As shown in Figure 8.13a, the channels of the devices are printed with MoS_2 inks (terpineol as the solvent and EC as the stabilizing polymer) and the electrode is printed with commercial silver inks. Even without any additional device engineering, the simple devices have already exhibited rapid response to the switching of any illumination ranging from ultraviolet to infrared light. As shown in Figure 8.13b,c, upon every illumination (dimming), a unique peak (valley) appears in the current–time curves. The peaks and valleys are likely generated by the correlation between the intrinsic photoresponse of MoS_2 and the trapping/detrapping process in the printed MoS_2 films. The responsivity reaches the level of $40 \mu\text{A W}^{-1}$, and the response time is less than 0.6 s (Figure 8.13c).

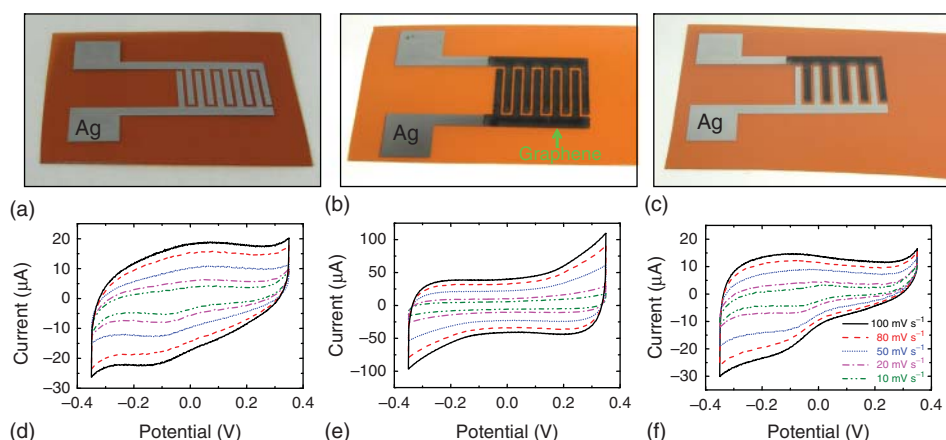


Figure 8.12 Inkjet-printed mSCs on Kapton with graphene electrodes. (a) Printed silver current collectors. (b) Printed graphene electrodes (eight printing layers) on top of silver current collectors. (c) Asymmetric supercapacitors where only one set of silver figures is covered by printed graphene (four printing layers). All the fingers are 1.0 mm wide, 9.4 mm long, and interspaced by 0.6 mm. (d–f) CV curves measured in 1 M Na_2SO_4 aqueous solutions for (a), (b), and (c), respectively. (Li *et al.* (2014) [20]. Reproduced with permission of Wiley.)

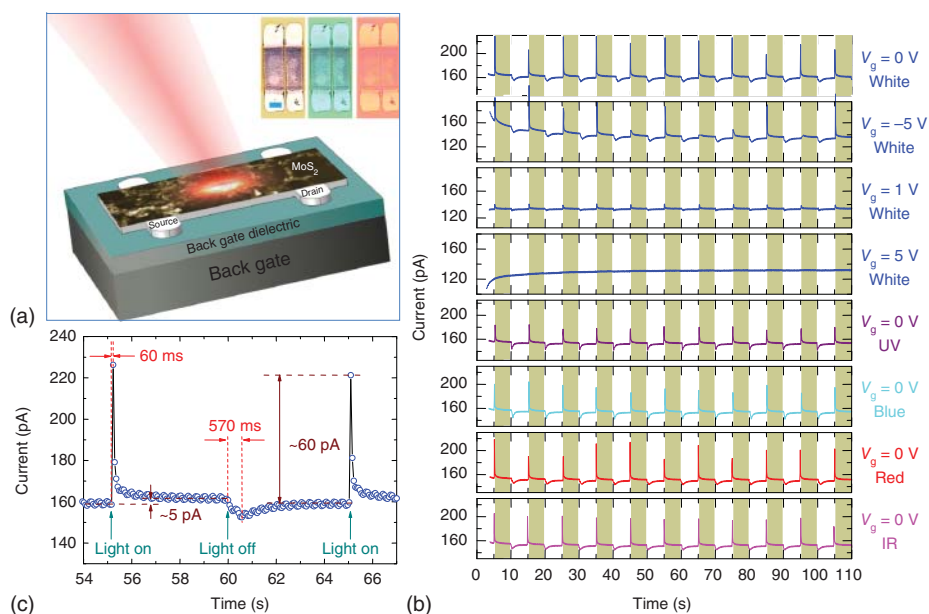


Figure 8.13 Photoresponse of a printed MoS_2 device (channel length is 13 μm). (a) Illustration of the MoS_2 device structure under illumination. Upper-right inset: optical micrographs of the device under different illuminations of white (left), blue (middle), and red (right) lights. The scale bar is 100 μm . (b) Time-resolved photoresponse of the device under different gate bias V_g and/or different illuminations. The lights are on (off) in the shaded (unshaded) intervals. Each interval is 5 s. (c) A close-up view of the photoresponse to white light at $V_g = 0$ V [the topmost one in (b)]. In all measurements, the drain voltage is $V_d = 1$ V. (Li *et al.* (2014) [21]. Reproduced with permission of Wiley.)

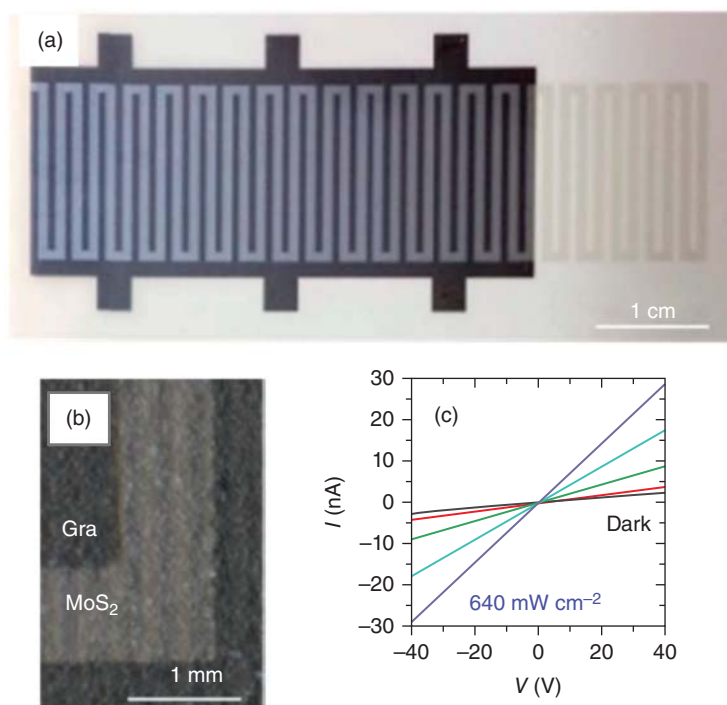


Figure 8.14 Inkjet-printed all-2D-material photodetectors. (a) Photograph of one device with interdigitated graphene electrode (black region) and zigzag MoS₂ channel (yellow region). (b) An optical image showing the graphene/MoS₂ interface. (c) Current–voltage curves for the device in dark and under different illuminations. (Finn *et al.* (2014) [17]. Reproduced with permission of Royal Society of Chemistry.)

As shown in Figure 8.14, Finn *et al.* [17] printed all-2D-material photodetectors where the electrodes (interdigitated structure) are printed with graphene inks and the channels (zigzag structures) are printed with MoS₂ inks. Both graphene and MoS₂ inks are binder free with NMP as the solvents. When illuminated at an incident laser (wavelength 532 nm), considerable photocurrent can be observed (Figure 8.14).

8.3.4 Solar Cells

It is reported that the graphene edges exhibit faster electron transfer rate and stronger electrocatalytic activity than graphene basal planes [38]. Therefore, exfoliated graphene nanosheets may offer good electrocatalytic properties, which, in addition to the electrical conductivity and chemical stability, make graphene an attractive counter-electrode material. Dodoo-Arhin *et al.* [23] used graphene inks (isopropanol as the solvent and PVP as the binder) to print counter-electrodes for natural and ruthenium-based dye-sensitized solar cells. The repeatability of the printing process enables the printing of uniform

counter-electrodes, with $\sim 5\%$ standard deviation in the sheet resistance. In the case of natural dyes, the conversion efficiency of the devices with the printed graphene counter-electrodes is $\sim 3.0\%$, comparable to $\sim 4.4\%$ efficiency for those using platinum (Pt) counter-electrodes. For the ruthenium-based dye, the inkjet-printed graphene counter-electrode shows a $\sim 3.0\%$ conversion efficiency, comparable to $\sim 4.4\%$ obtained using Pt counter-electrodes. These results suggest inkjet-printed graphene provides a cost-efficient alternative to replace the expensive Pt counter-electrodes in solar cell applications.

8.4 Discussion and Outlook

In this chapter, we reviewed the present status and challenges of the research on inkjet printing of graphene and 2D materials-based thin films. We systematically introduced the printing procedure, including ink formulation, jetting and patterning, ink drying, and posttreatments. Several promising applications based on printed 2D material thin films were also discussed.

Based on the introduction in this chapter, one can see great progress has been demonstrated in the past several years in this relevant field. Various efficient and stable inkjet printing inks have been developed for graphene and other 2D materials in the literature. The inks enable reliable jetting and patterning at high resolutions up to $50\text{ }\mu\text{m}$. Different strategies are implemented to suppress the coffee-ring effect during ink drying. During posttreatments, in addition to the traditional thermal annealing or sintering, advanced techniques, such as laser annealing, have also been developed to further improve the quality of printed 2D material thin films. A variety of promising applications have been demonstrated, including transparent conductors, micro-supercapacitors, photodetectors, solar cells, and so on.

However, the techniques of inkjet-printed 2D material thin films are still in infancy. Considerable efforts are anticipated to be made in the field in order to scale up the techniques and further extend the applications. Here, we forecast several research tendencies in the near future: (i) innovative ink composition will be developed to attain efficient, reliable, sintering-free, and environmentally friendly inkjet printable inks for 2D materials. At present, the binder-containing inks can be environmentally friendly but suffer from the need of high-temperature annealing. The binder-free inks are free from annealing or sintering but are often toxic. Innovative ink composition and formulation techniques that simultaneously address the issues are desired to enable the printing on arbitrary substrates and scale-up techniques for industrial manufacturing. (ii) Scalable exfoliation techniques will be integrated into ink formulation to improve the quality of 2D materials in the inks. So far, the nanosheets in the 2D material inks typically comprise more than 5 flake layers. In order to improve the performance of the printed 2D materials, emerging exfoliation techniques, such as electrochemical exfoliation, shear exfoliation, and expanded graphene, will be employed to produce high-quality 2D materials (with monolayer or few

(<3) layers) as the starting materials. (iii) Inks of more and more 2D materials will be formulated and applied in printed electronics. To date, the 2D material inks only focus on a few types of materials, such as graphene and MoS₂. With the continuous discovery or synthesis of innovative 2D materials, more and more high-performance and multifunctional 2D materials will be available in the field and greatly extend the applications. (iv) The printing processes, including printing, drying, and posttreatments, will be improved (or replaced by novel techniques) to fabricate highly uniform thin films and obtain high-performance devices. (v) Innovative applications will be developed making best of the direct patterning merits of inkjet printing and unique properties of 2D materials.

Acknowledgments

We acknowledge the financial support by the Swedish Research Council through the Framework project (No. 2014–6160) and the Marie Skłodowska Curie International Career Grant (No. 2015–00395, co-funded by Marie Skłodowska-Curie Actions FP7, through the Project INCA 600398), the European Research Council through the Proof of Concept Grant iPUBLIC (No. 641416), the Göran Gustafsson Foundation through the Young Researcher Prize (No. 1415B), the Olle Engkvist Byggmästare Foundation through the Research Project (No. 2014/799), and the Swedish Innovation Agency VINNOVA through the Strategic Innovation Program for Graphene, iEnergy (No. 2015–01337).

References

- 1 Rees, F. (2006) *Johannes Gutenberg: Inventor of the Printing Press*, Compass Point Books.
- 2 Choi, H.W., Zhou, T., Singh, M., and Jabbour, G.E. (2014) Recent developments and directions in printed nanomaterials. *Nanoscale*, **7**, 3338–3355. doi: 10.1039/c4nr03915g
- 3 Singh, M., Haverinen, H.M., Dhagat, P., and Jabbour, G.E. (2010) Inkjet printing-process and its applications. *Adv. Mater.*, **22**, 673–685. doi: 10.1002/adma.200901141
- 4 Organic Electronics Association (2011) *OE-A Roadmap for Organic and Printed Electronics*, Organic Electronics Association, Frankfurt.
- 5 Novoselov, K.S., Fal'ko, V.I., Colombo, L., Gellert, P.R., Schwab, M.G., and Kim, K. (2012) A roadmap for graphene. *Nature*, **490**, 192–200. doi: 10.1038/nature11458
- 6 Coleman, J.N., Lotya, M., O'Neill, A., Bergin, S.D., King, P.J., Khan, U. *et al.* (2011) Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science*, **331**, 568–571. doi: 10.1126/science.1194975
- 7 Yang, S., Brüller, S., Wu, Z.S., Liu, Z., Parvez, K., Dong, R. *et al.* (2015) Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene. *J. Am. Chem. Soc.*, **137**, 13927–13932. doi: 10.1021/jacs.5b09000

- 8 Paton, K.R., Varrla, E., Backes, C., Smith, R.J., Khan, U., O'Neill, A. *et al.* (2014) Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.*, **13**, 624–630. doi: 10.1038/nmat3944
- 9 Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M., and Chhowalla, M. (2011) Photoluminescence from chemically exfoliated MoS₂. *Nano Lett.*, **11**, 5111–5116. doi: 10.1021/nl201874w
- 10 Wang, Q.H., Kalantar-Zadeh, K., Kis, A., Coleman, J.N., and Strano, M.S. (2012) Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.*, **7**, 699–712. doi: 10.1038/nnano.2012.193
- 11 Huang, X., Leng, T., Zhang, X., Chen, J.C., Chang, K.H., Geim, A.K. *et al.* (2015) Binder-free highly conductive graphene laminate for low cost printed radio frequency applications. *Appl. Phys. Lett.*, **106**, 203105. doi: 10.1063/1.4919935
- 12 Majee, S., Song, M., Zhang, S.-L., and Zhang, Z.-B. (2016) Scalable inkjet printing of shear-exfoliated graphene transparent conductive films. *Carbon*, **102**, 51–57. doi: 10.1016/j.carbon.2016.02.013
- 13 Torrisi, F., Hasan, T., Wu, W.P., Sun, Z.P., Lombardo, A., Kulmala, T.S. *et al.* (2012) Inkjet-printed graphene electronics. *ACS Nano.*, **6**, 2992–3006. doi: 10.1021/nn2044609
- 14 Zhou, K.-G., Mao, N.-N., Wang, H.-X., Peng, Y., and Zhang, H.-L. (2011) A mixed-solvent strategy for efficient exfoliation of inorganic graphene analogues. *Angew. Chem., Int. Ed. Engl.*, **50**, 10839–10842. doi: 10.1002/anie.201105364
- 15 Yi, M., Shen, Z., Ma, S., and Zhang, X. (2012) A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite. *J. Nanopart. Res.*, **14**, 1003. doi: 10.1007/s11051-012-1003-5
- 16 Capasso, A., Del Rio Castillo, A.E., Sun, H., Ansaldi, A., Pellegrini, V., and Bonaccorso, F. (2015) Ink-jet printing of graphene for flexible electronics: An environmentally-friendly approach. *Solid State Commun.*, **224**, 53–63. doi: 10.1016/j.ssc.2015.08.011
- 17 Finn, D.J., Lotya, M., Cunningham, G., Smith, R.J., McCloskey, D., Donegan, J.F. *et al.* (2014) Inkjet deposition of liquid-exfoliated graphene and MoS₂ nanosheets for printed device applications. *J. Mater. Chem. C*, **2**, 925–932. doi: 10.1039/C3TC31993H
- 18 Secor, E.B., Prabhuramirashi, P.L., Puntambekar, K., Geier, M.L., and Hersam, M.C. (2013) Inkjet printing of high conductivity, flexible graphene patterns. *J. Phys. Chem. Lett.*, **4**, 1347–1351. doi: 10.1021/jz400644c
- 19 Li, J., Ye, F., Vaziri, S., Muhammed, M., Lemme, M.C., and Östling, M. (2013) Efficient inkjet printing of graphene. *Adv. Mater.*, **25**, 3985–3992. doi: 10.1002/adma.201300361
- 20 Li, J., Lemme, M.C., and Östling, M. (2014) Inkjet printing of 2D layered materials. *ChemPhysChem*, **15**, 3427–3434. doi: 10.1002/cphc.201402103
- 21 Li, J., Naiini, M.M., Vaziri, S., Lemme, M.C., and Östling, M. (2014) Inkjet printing of MoS₂. *Adv. Funct. Mater.*, **24**, 6524–6531. doi: 10.1002/adfm.201400984

- 22 Gao, Y., Shi, W., Wang, W., Leng, Y., and Zhao, Y. (2014) Inkjet printing patterns of highly conductive pristine graphene on flexible substrates. *Ind. Eng. Chem. Res.*, **53**, 16777–16784. doi: 10.1021/ie502675z
- 23 Dodoo-Arhin, D., Howe, R.C.T., Hu, G., Zhang, Y., Hiralal, P., Bello, A. *et al.* (2016) Inkjet-printed graphene electrodes for dye-sensitized solar cells. *Carbon*, **105**, 33–41. doi: 10.1016/j.carbon.2016.04.012
- 24 Liang, Y.T. and Hersam, M.C. (2010) Highly concentrated graphene solutions via polymer enhanced solvent exfoliation and iterative solvent exchange. *J. Am. Chem. Soc.*, **132**, 17661–17663. doi: 10.1021/ja107661g
- 25 Li, J., Ye, F., Vaziri, S., Muhammed, M., Lemme, M.C., and Östling, M. (2012) A simple route towards high-concentration surfactant-free graphene dispersions. *Carbon*, **50**, 3113–3116. doi: 10.1016/j.carbon.2012.03.011
- 26 Kuang, M., Wang, L., and Song, Y. (2014) Controllable printing droplets for high-resolution patterns. *Adv. Mater.*, **26**, 6950–6958. doi: 10.1002/adma.201305416
- 27 Soltman, D. and Subramanian, V. (2008) Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir*, **24**, 2224–2431. doi: 10.1021/la7026847
- 28 Deegan, R.D., Bakajin, O., and Dupont, T.F. (1997) Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, **389**, 827–829.
- 29 Kuang, M., Wang, J., Bao, B., Li, F., Wang, L., Jiang, L. *et al.* (2014) Inkjet printing patterned photonic crystal domes for wide viewing-angle displays by controlling the sliding three phase contact line. *Adv. Opt. Mater.*, **2**, 34–38. doi: 10.1002/adom.201300369
- 30 Yunker, P.J., Still, T., Lohr, M.a., and Yodh, a.G. (2011) Suppression of the coffee-ring effect by shape-dependent capillary interactions. *Nature*, **476**, 308–311. doi: 10.1038/nature10344
- 31 Kim, D., Jeong, S., Park, B.K., and Moon, J. (2006) Direct writing of silver conductive patterns: Improvement of film morphology and conductance by controlling solvent compositions. *Appl. Phys. Lett.*, **89**, 264101, doi: 10.1063/1.2424671
- 32 Del, S.K., Bornemann, R., Bablich, A., Schäfer-Eberwein, H., Li, J., Kowald, T. *et al.* (2015) Optimizing the optical and electrical properties of graphene ink thin films by laser-annealing. *2D Mater.*, **2**, 011003. doi: 10.1088/2053-1583/2/1/011003
- 33 Li, J. and Östling, M. (2013) Prevention of graphene restacking for performance boost of supercapacitors—a review. *Crystals*, **3**, 163–190. doi: 10.3390/cryst3010163
- 34 Wu, Z.S., Feng, X., and Cheng, H.M. (2014) Recent advances in graphene-based planar micro-supercapacitors for on-chip energy storage. *Natl. Sci. Rev.*, **1**, 277–292. doi: 10.1093/nsr/nwt003
- 35 Gao, W., Singh, N., Song, L., Liu, Z., Reddy, A.L.M., Ci, L. *et al.* (2011) Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.*, **6**, 496–500. doi: 10.1038/nnano.2011.110

- 36 Liu, C.-H., Chang, Y.-C., Norris, T.B., and Zhong, Z. (2014) Graphene photodetectors with ultra-broadband and high responsivity at room temperature. *Nat. Nanotechnol.*, **9**, 273–278. doi: 10.1038/nnano.2014.31
- 37 Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A., and Kis, A. (2013) Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.*, **8**, 497–501. doi: 10.1038/nnano.2013.100
- 38 Yuan, W., Zhou, Y., Li, Y., Li, C., Peng, H., Zhang, J. *et al.* (2013) The edge- and basal-plane-specific electrochemistry of a single-layer graphene sheet. *Sci. Rep.*, **3**, 2248. doi: 10.1038/srep02248

9

Inkjet Printing of Photonic Crystals

Minxuan Kuang and Yanlin Song

9.1 Introduction

Photonic crystals (PCs) have attracted widespread interest during the past decades owing to their special light manipulation properties and potential applications in various optical devices [1–14]. In particular, patterned PCs are especially important due to the extensive applications in sensing arrays [15–19], light waveguides [3, 4], full-color displays, and so on [6, 8, 20–22]. Traditional PC patterning methods include light lithography [6] or template assembly [7, 16, 17]. Several restrictions exist in the traditional methods such as complex fabricating process, limited pattern design, or requiring expensive apparatus. Inkjet printing technique, with the advantage of flexibility, low cost, and high-throughput output, has become one of the most promising candidates of patterning various materials [23–39]. Inkjet printing technique has been proved effective for fabricating PC patterns by combining direct writing and particle self-assembly within the droplet [20, 40–44], which is regarded to be promising for the fabrication of microstructures for the next-generation photonic and display devices.

The basic elements of determining the quality of inkjet-printed PC patterns include the latex assembly structure within each printed droplet and the deposition pattern. The latex assembly structure and the deposition pattern usually are influenced by the substrate wettability and ink formulation. The substrate wettability including static or dynamic contact angle (CA) affects the deposited morphology and evaporation mode of the printed ink droplets, which further governs the shape and size of ink droplets. The ink formulation affects the viscosity, surface tension of the inks, and the capillary flow within the droplet, which influence the printing process and the particle assembly structures. All of these factors have combinative influences on the printed PC patterns and their optical properties. In this chapter, the process of inkjet printing, the behaviors of droplets on substrate, the influence of substrate wettability and ink formulation on the inkjet-printed PC dots or lines, and suppression of “coffee-ring” effect are discussed. The typical applications of inkjet-printed PCs are also discussed. In the last section, some promising research directions for the inkjet printing of PCs are listed.

9.2 Inkjet Printing of Photonic Crystals

9.2.1 Process of Inkjet Printing

Inkjet printing is a deposition technique based on drop-on-demand and continuous drops jetting technique, which usually uses liquid materials consisting of solutes, solvents, and additives as inks. An inkjet printer usually has tens to hundreds of nozzles and can eject 6000 droplets per second. Therefore, the patterning efficiency of inkjet printing technique is very high. Understanding the printing process is necessary for effectively fabricating high-quality PC patterns and devices. A typical process of printing PCs essentially involves the ejection of a fixed quantity of colloidal droplets from a nozzle via piezoelectric action, followed by the impaction and deposition of the droplet on substrate. As shown in Figure 9.1a, colloidal droplets are formed and ejected by propagating a piezoelectric pulse in the liquid contained in a chamber. The droplet size is usually in the range of 10–50 μm , which depends on the nozzle diameter and the applied piezoelectric pulse [45–47]. After ejecting from the nozzles, the droplets fall under the actions of gravity and air resistance until they impact and spread on a substrate. The colloidal droplets then dry after solvent evaporation, along with the self-assembly of the contained colloids into a well-ordered arrangement. In general, the impacting behavior of the ink droplets is divided into two stages (Figure 9.1b) [48]. In the first stage, inertial force dominates the impacting process, followed by impact-driven spreading. At the later stage, the capillary forces tend to dominate. Droplet spreading is controlled by the capillary process, in which the recoiling, oscillation, and extension may occur.

The behavior of ink droplets on the substrate depends mainly on the surface wettability and the velocity of the droplets. When an ink droplet is gently dipped

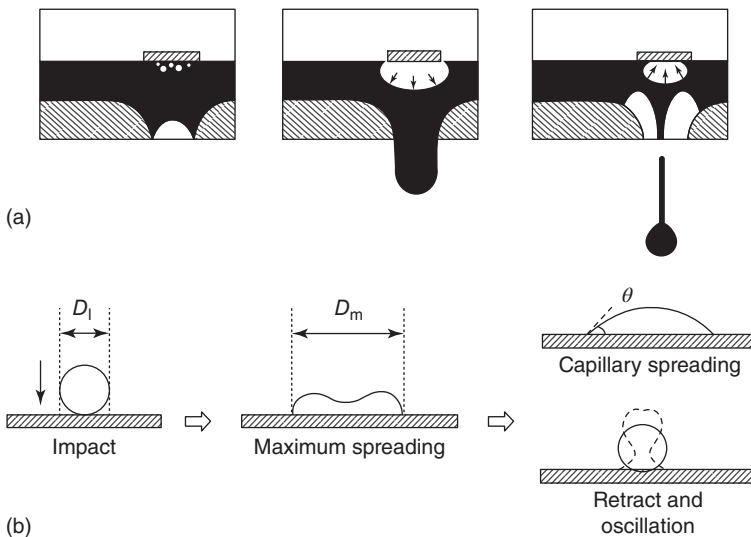


Figure 9.1 (a) Generation process of the ink droplets. (b) Schematic illustration of the droplet behaviors after impacting the substrate.

on the substrate without any velocity, the gas, liquid, and solid phases are able to reach a balance state quickly. This balance state is usually characterized by contact angle (θ). In the case of $\theta = 0$, the droplet spreads to form a very thin film, even form a single-molecule layer theoretically. In the case of $\theta > 0$, sessile droplets sit on the substrate under the combined action of the gravity of droplet and the surface energy of three phases. The balance θ is closely related to the surface energy according to Yang's equation (Equation 9.1).

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (9.1)$$

where γ_{SG} , γ_{SL} , and γ_{LG} are the surface tension of solid–gas phase, solid–liquid phase, and liquid–gas phase, respectively.

However, the ink drops jetting from the printer have high velocity before they impact the substrate. Because the velocity of jetted ink droplet is as high as 10 m s^{-1} , the droplet deforms significantly during impacting. In the impacting process, the kinetic energy converts into deformation energy and surface energy. The stored deformation energy enables the ink droplet retracting or even entirely bouncing from the surface in the case of low surface energy [49, 50]. Therefore, the process of these drops reaching balance is more complicated, where the effect of velocity (inertia) has to be considered. The kinetic energy of the drops becomes a key factor affecting the subsequent impacting behavior. During the impacting process, different phenomena occur depending on the substrate wettability and the jetting velocity of the drops. There are three most common phenomena: spreading, bouncing, and splashing. When a jetted ink droplet impacts a wetting substrate, it spreads to a disk under the action of inertia [51]. Then, the three-phase contact line (TCL) undergoes oscillatory motion of advancing and receding to dissipate the kinetic energy, which is finally suppressed by the viscosity of the drop and the adhesion between the drop and substrate [52]. The time needed for the drops to reach a balance state depends on the size of the droplets. Several milliseconds are needed for the millimeter-sized drops, while only several microseconds are needed for the micrometer-sized drops. The final shape of the sessile drop is determined by the water contact angle on the substrate. When a jetted ink droplet impacts a nonwetting substrate, the droplet retracts after it spreads to the maximum dimension and even bouncing from the substrate due to the extremely low adhesion between the drop and substrate [49, 53]. Besides spreading and bouncing, splashing is likely to occur when an ink droplet impacts a substrate with roughness at high speed [54, 55]. This splashing behavior generates satellite drops, lowering the printing quality. There is always a threshold for the transition from spreading to splashing, where the initial kinetic energy plays a key role. The velocity of the drops, surface roughness [55–57], drop size, the atmospheric pressure and other properties determine whether splashing happens. The process of drops impacting solid surface has attracted widespread interest 100 years ago. Studying this phenomenon will promote the development of inkjet printing technology. The behavior of spreading, bouncing, and splashing greatly affects the morphology of printed PCs. Regulating the impacting process of ink drops is significant for fabricating advanced PC devices from inkjet printing.

9.2.2 Inkjet Printing of Fine Controlled PC Dots and Lines

9.2.2.1 Influence of the Ink Formulation

One of the major challenges in inkjet printing technique is to develop ink materials and formulations, which not only affects the ejecting process but also dictates the quality of the printed patterns and the performance of as-obtained devices. In general, an ink formulation for printing PCs contains colloidal particles, solvents, and additives. The constituents and their corresponding dosage are critical for the formulation. Monodispersed particles, dispersion stability, appropriate viscosity, and surface tension are essential for inkjet-printed high-quality PC patterns and devices. As for a typical ink formulation of printing PCs, monodispersed colloidal particles without any aggregation are crucial for attaining high dispersion stability, avoiding nozzle clogging, and obtaining well-ordered assembly. For example, the colloidal particles with a polydispersity of 0.005 favor the assembling of long-range periodic structures [20]. Monodispersed colloidal particles can be obtained by emulsion polymerization [58, 59], dispersion polymerization [60], Stöbersynthesis [61], and hydrothermal synthesis [62], and so on. The diameters of the particles are tuned by the synthetic conditions. The synthesized monodispersed colloidal particles are then added into diluent solvent to attain the required concentration. The solvents in formulation are multiple components that are used to meet the requirements of dispersion stability, particle assembly, as well as to adjust the viscosity and surface tension of inks. The main solvent is a good dispersant for the colloidal particles. The printing ink should remain stable without precipitation for at least 6 months. Secondary solvents such as ethylene glycol, *N,N*-dimethylformamide, glycerol, diethylene glycol, or acetophenone, which have high boiling point and low surface tension, are added to regulate the wetting behavior, evaporation mode, and drying time of the printed ink droplets. These solvents can alter the deposition pattern of ink droplet and suppress the “coffee-ring” effect by generating Marangoni flow derived from their high boiling point and low surface tension. When the secondary solvent is added, an additional surface tension gradient is produced by the concentration gradient of the solvent component between the center and edge of the droplet. This additional surface tension gradient drives the fluid flow inward. In addition, the utilization of the secondary solvent with high boiling point can prolong evaporation time, facilitating particles assembling into well-ordered structures. Other solvents (such as ethanol) or additives (such as surfactants) are also formulated into the inks to regulate the viscosity and surface tension of the inks. In general, an ink formulation with a viscosity of 8–14 cPs and surface tension of 25–40 dyn cm⁻¹ is desired for a fluent printing process.

As mentioned earlier, the particle assembly structure is critical for the optical property of PCs. It is found that particle assembly structure within the printed droplets varies depending upon the ink formulation. A formulation containing single solvent usually leads to a ring-like deposition and poor ordering of particles as shown in Figure 9.2a [63]. In this case, the particle distribution is uneven, where most particles are aggregated at the periphery and a few particles are scattered in the center. Only a small part of particles at the periphery assemble into ordered structures. The particles in the center are randomly scattered without any

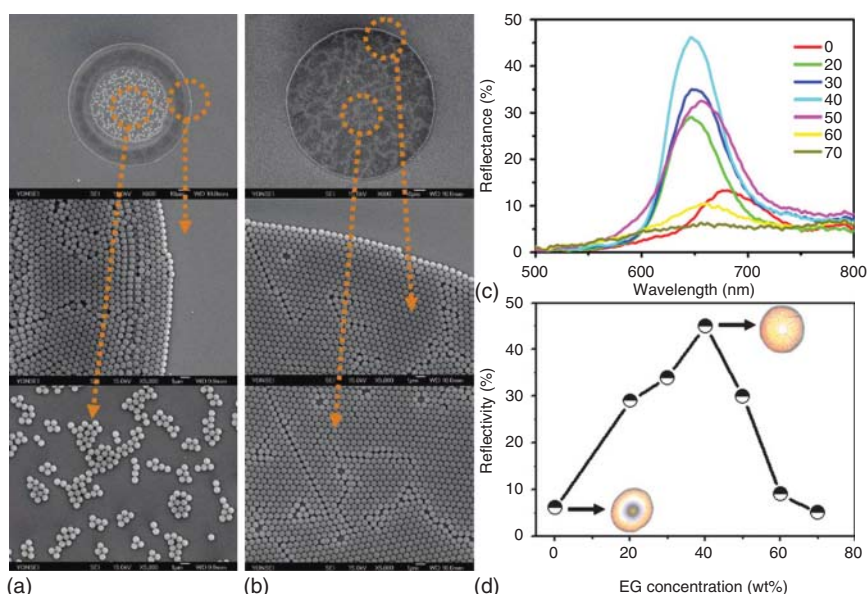


Figure 9.2 Influence of ink composition on the particle deposition and assembly structure. SEM images of particle deposition printed from (a) water-based ink and (b) water/formamide-based ink; (Park and Moon (2006) [63]. Reproduced with permission of American Chemical Society.) (c,d) Optical properties of the printed PC dots from inks with varying ethyl glycol content. (Cui *et al.* (2009) [20]. Reproduced with permission of Royal Society of Chemistry.)

ordered structure. Therefore, the optical property of such assembly structures is very poor. In contrast, a formulation containing mixed solvent gives rise to uniform dot-like deposition. For example, in the case of the water/formamide-based ink droplet, a complete self-assembled monolayer of particles with well-ordered structure in the dot-like deposition is obtained (Figure 9.2b) [63]. The alternation of deposition pattern is mainly attributed to the inward Marangoni flow directing to the center of the droplet. This inward flow counters the outward convective flow and results in homogeneous colloidal crystals without distinct ring-shaped deposition. Similarly, introducing ethylene glycol to water-based inks could also result in homogeneous colloidal crystals. As shown in Figure 9.2c,d, the deposition morphology changes from ring-like pattern to dot-like pattern with the dosage of ethylene glycol increasing to 40%. But further increasing the dosage of ethylene glycol reduces the order degree of the particles. Correspondingly, the reflecting strength of the printed PC dots reaches the peak when the dosage of ethylene glycol is 40% [20].

The colloidal particle concentration is another important factor to the particle assembly morphology and the optical property of PCs. Researchers have found that, for the water/formamide mixed-solvent-based ink with 0.5 vol% particles, most of the particles are deposited at the periphery of the droplet, while a few particle aggregates are randomly scattered in the center of the droplet. As the

particle concentration increases, the ring width becomes thicker and eventually forms a dot-like monolayer colloidal crystal at 4 vol%. The self-assembled monolayer colloidal crystal consists of large grains of well-ordered hexagonal lattice of particles, with several point and line defects inside. Further increasing the concentration above 4 vol%, the similar dot-like deposit is produced but either double or multiple particle layers occur in the central region [63].

Introducing functional monomers into the ink formulation produces a positive effect on printing PCs with uniform deposition and well-ordered particle assembly. Acrylamide, acrylic acid, and *N*-isopropyl acrylamide are the commonly used functional monomers [41, 64]. The introduction of these monomers regulates the surface tension of the printing inks, and the polymerization of these monomers increases the viscosity of printed drops. The character change of the printing inks alters the wetting and spreading behavior of the ink droplets as well as the assembly process of the particles. The dosage and polymerization rate of the monomers play a critical role in the particle assembly and the resulting deposition pattern of ink droplets. A perfect match between the polymerization rate and particle assembly rate results in PCs with homogeneous deposition and well-ordered particle arrangement. When the particle assembly rate is faster than the monomer polymerization rate, the particles adapt a ring-like deposition because the ink viscosity is not high enough to resist the particles migrating to the edge of the droplet. When the monomer polymerization rate is faster than the particle assembly rate, there is not enough time for the particles to assemble into ordered particles due to the rapid increasing ink viscosity. In this case, the printed PC dots show a relatively low reflection strength and faint structure color [41].

9.2.2.2 Influence of Substrate Wettability

In a typical printing process, uniform-sized ink drops are rapidly produced and deposited on arbitrary substrates. Colloidal particles contained in each drop undergo self-assembly during evaporation, forming PC dots or lines with ordered structure. During this process, the wettability of substrates plays a critical role in the morphology and assembly structure of printed PC dots or lines. It influences the assembly time, the assembly interaction force, and the colloid migration. Specifically, the static wettability of the substrates usually determines the equilibrium size and shape of printed PCs. In contrast, the dynamic wettability of the substrates always controls the wetting and dewetting behaviors of printed drops [65–70] and further governs the evaporating mode of drops and the resultant shape and structure of the PC dots or lines.

The static wettability is characterized by apparent contact angle, usually termed as hydrophilic or hydrophobic. The different surface nature gives rise to distinct drop shapes on substrates. On a hydrophilic substrate with very low contact angle, the ink drops have a tendency to spread on surfaces and form disk-like ink drops, and a higher contact angle leads to cap-like drops. In contrast, the ink drops printed on a hydrophobic substrate form a hemispherical shape. Compared to the disk- or cap-like ink drops printed on the hydrophilic substrate, the hemispherical-shaped drops have thicker liquid layer, allowing slower evaporation and longer assembly time. Figure 9.3 illustrates the influence

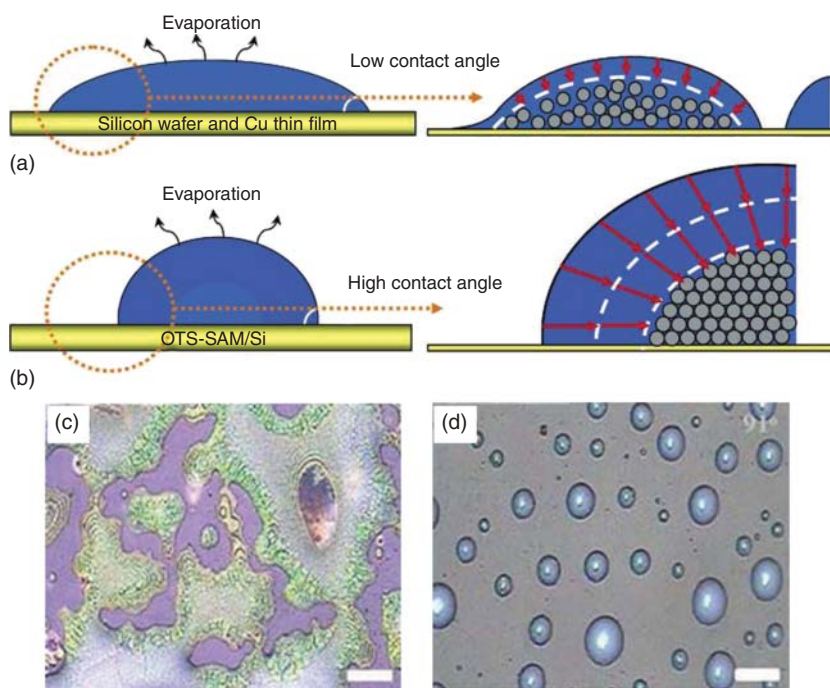


Figure 9.3 (a,b) Schematic illustration of colloidal particles' assembly with a droplet printed on the (a) hydrophilic and (b) hydrophobic substrate. (Ko *et al.* (2004) [71]. Reproduced with permission of American Chemical Society.) (c,d) Optical images of the printed PC dots on substrate with different water contact angles: (c) 48° and (d) 91°.

of substrate wettability on the shape and particle assembly structure of printed PC dots [20, 71]. Figure 9.3c displays the optical microscopy images of the colloidal ink drops printed on the hydrophilic substrate. Irregular flat disk- and ring-like structures are formed. The ink drop on the hydrophilic substrate with low contact angle forms a very thin liquid layer at the edge. Thus, the evaporation rate at the periphery is much faster than that at the center. An outward capillary flow is induced and drives the colloidal particles moving to the edge. This prevents the TCL of the ink drop from receding, so the contact angle gradually decreases and the base diameter remains consistent on the surface. In this case, the colloidal particles suspended in the printed drops are drawn to the drying front to replenish the liquid removed from the edge. Such a drying mode of drops results in a random deposition in flat ring-like shape of colloidal particles. In contrast, the printed colloidal drop on hydrophobic substrate retains a hemispherical shape, and the TCL retracts as the droplet shrinks. The colloidal particles in the evaporating drop are gradually concentrated as the solvent slowly vaporizes. When the particle concentration reaches a critical value at which their mobility is significantly reduced, the colloidal particles start to crystallize at the liquid surface. Finally, a colloidal crystal with compact assembly structure is grown (Figure 9.3d). The colloidal particles are arranged in a long-range ordered

structure, displaying large domains of hexagonally packed particles with a few point and line defects. The obtained PC dots on such substrates show good optical properties.

The dynamic wettability of substrates is usually evaluated by the advancing contact angle, the receding contact angle, the hysteresis contact angle, or the adhesion force of the liquid droplet on the substrate. It influences the evaporating mode of drops, the assembly time, the assembly interaction force, and the colloid migration. Exhaustive studies have been carried out on the evaporation process of water droplets and the particle assembly structures on substrates with different wettabilities [43, 72–75]. The researches show that the droplet evaporating on superhydrophobic substrates with high hysteresis contact angle or low hysteresis experiences totally different evaporation modes [76]. On substrates with high hysteresis, the water droplets follow an evaporation mode similar to that on smooth hydrophilic substrates due to the pinning behavior of TCL on the substrate, where the contact base dimension remains consistent and the contact angle gradually decreases. In contrast, the TCL of the droplet continuously recedes and the contact angle almost remains unchanged during the evaporation process on substrates with low hysteresis. The difference in the TCL motion (pinning or receding behavior) produces a profound influence on the lifetime of the droplets. The lifetime of droplets on substrates with low hysteresis contact angle is much longer than on that substrates with high hysteresis contact angle, because high values of contact angles higher than 90° are sustained on such a surface for much longer time and the evaporation rate of droplets is likely to be suppressed due to the local saturation vapor near the TCL. Different wetting hysteresis of droplets on the substrate gives rise to distinct latex assembly structures. The substrate with low hysteresis contact angle always indicates low adhesion force of water droplet on surface. The low-adhesive substrate has a positive effect on the well-ordered assembly structure. Perfect well-ordered, crack-free PCs are obtained on a low-adhesive superhydrophobic substrate (Figure 9.4a) [75]. First, the receding TCL of the latex droplet on the low-adhesive superhydrophobic substrate supplies enough evaporation time for the latex assembly, which is very beneficial for well-ordered latex assembly during the rapid evaporation process of the ink droplet. Second, the low-adhesive characteristic satisfies the free shrinking of the latex particles from the restriction of substrate during evaporation process, releasing the tensile stress and contributing to the crack-free assembly structure. Third, the continuously receding behavior of TCL squeezes the latex particles and results in compact structure with low air fraction. Such a perfect well-ordered, crack-free PC presents very narrow stopbands (12 nm). Besides the wetting hysteresis, receding contact angle also exerts significant influence on the latex particle assembly structures and the corresponding optical property of the printed PCs (Figure 9.4b–d) [43]. On a substrate with low receding CA of $18.0 \pm 5.7^\circ$, the particles partially assemble into ordered structure, and the reflection intensity of printed PC dots on such a substrate is weak. In contrast, the particles assemble into hexagonal ordered structure, and the PC dots exhibit strong reflection intensity on a substrate with receding CA of $93.3 \pm 1.9^\circ$. The PC microdots show nearly uniform-sized, dome-shaped colloidal aggregates. Due to the continuously sliding behavior of TCL, latex particles

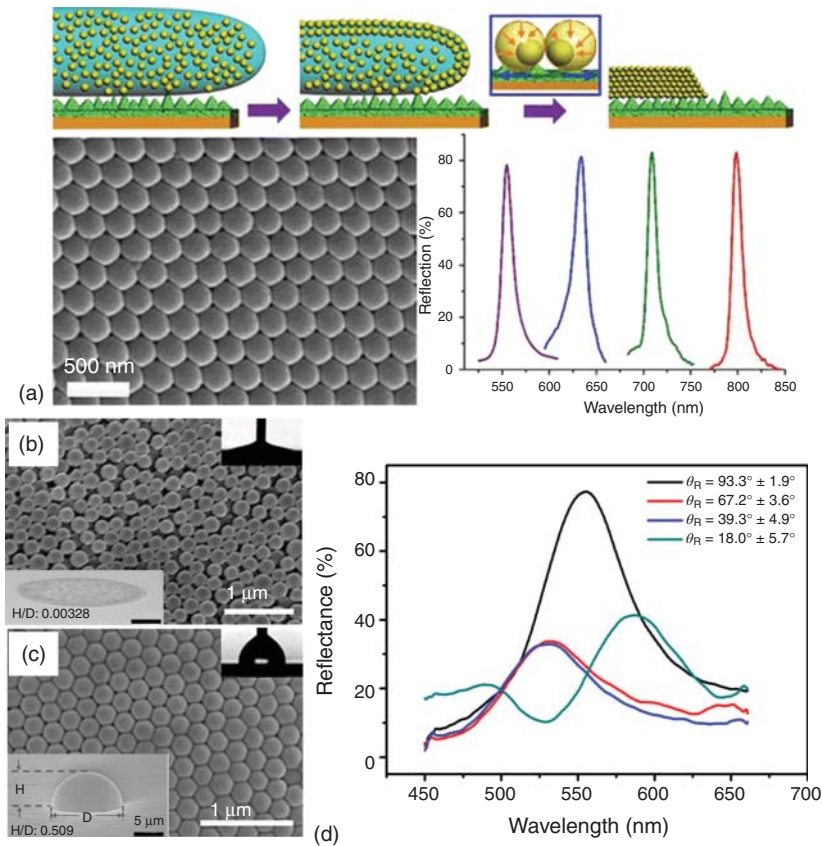


Figure 9.4 (a) Colloidal droplets on superhydrophobic substrate with low-adhesion-generating PCs with narrow stopband. (Huang *et al.* (2012) [75]. Reproduced with permission of American Chemical Society.) (b,c) SEM images of the particle assembly structure of printed PC dots on substrate with receding contact angle of (b) $18.0^\circ \pm 5.7^\circ$ and (c) $93.3^\circ \pm 1.9^\circ$. (d) The reflection intensity of printed PC dots on substrate with different receding contact angles. (Kuang *et al.* (2014) [43]. Reproduced with permission of Wiley.)

contained in each ink droplet are accumulated in the center of the droplet and assembled into compact-ordered structure, exhibiting good optical properties.

Compared with printing PC dots, inkjet printing of PC lines is more complicated and challenging. For practical applications, ideal inkjet-printed lines should be smooth, even, narrow, and straight. The coalescence of neighboring droplets directly affects the morphology of inkjet-printed lines. Many factors influence the droplet coalescence process, such as droplet space and delay time [29], drop surface tension [77], interfacial jamming of particles [78, 79], and surface dynamic wettability [80]. The droplet space and delay time are the most important factors (Figure 9.5a) [29]. If printed drops are too far apart to interact with each other (more than twice the radius of the drop), no coalescence occurs and isolated PC microdots are obtained. As the drop spacing decreases, isolated drops overlap but retain wavy contact lines, and a scalloped pattern emerges. Further decreasing

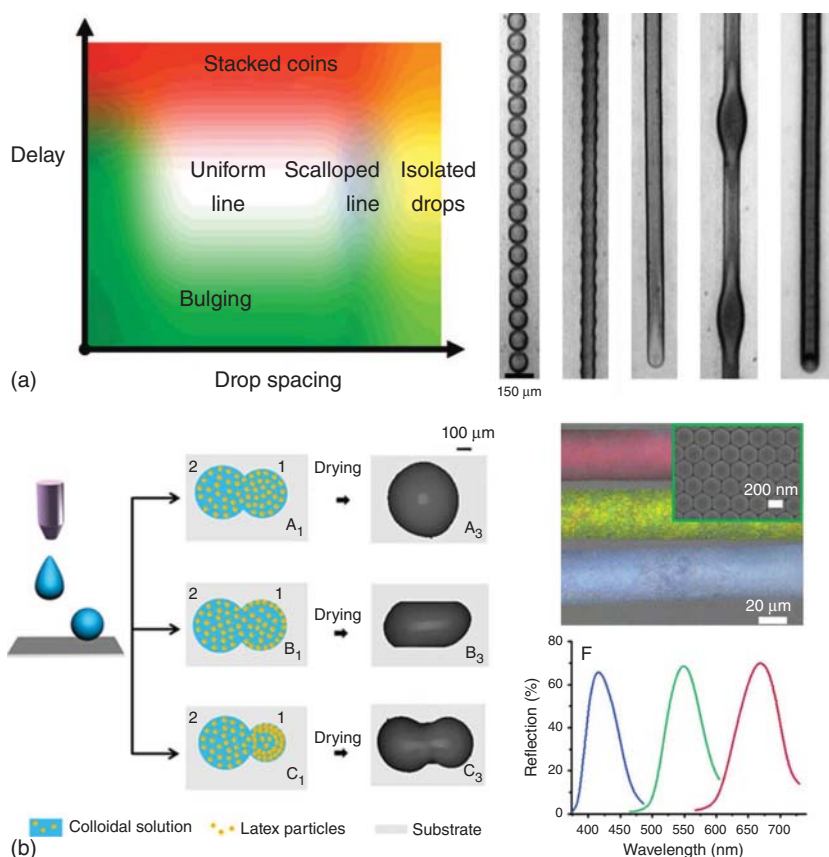


Figure 9.5 (a) The influence of the drop spacing and delay time on the morphology of printed droplets. Examples of printed line morphology: individual drops, scalloped, uniform, bulging, and stacked coins from left to right with decreasing drop spacing. (Soltman and Subramanian (2008) [29]. Reproduced with permission of American Chemical Society.) (b) Typical coalescing cases of the neighboring ink droplets induced by different dynamic wettabilities of ink droplets on the substrates. By adopting optimized dynamic wettability, straight and smooth PC lines with good optical property are obtained. (Liu *et al.* (2014) [80]. Reproduced with permission of American Chemical Society.)

the drop space eliminates the waving footprints and leads to a smooth straight line. Not only the drop space but also the suitable delay time is another prerequisite to realize homogeneous printing lines. When the delay time is too short, two neighboring droplets will coalesce into a larger one. But too long delay time leads to isolated drops due to the thick surrounding of the latex particle assembly. Another factor of surface wettability is also very important. On a hydrophobic substrate, line bulges always emerge due to the Rayleigh instability. These line bulges are undesired because they locally broaden the printed structures and damage the continuity of printed lines. A heated substrate is helpful to overcome this drawback. The increased temperature accelerates evaporation of the

solvent and increases the viscosity of liquids rapidly, which prevents the broadening of the lines [31]. In some cases, the surface dynamic wettability depends on the ink droplets' surface tension difference. By adjusting ink droplets' surface tension and the nanoparticle concentration, different dynamic wettabilities of ink droplets to substrates could be achieved and subsequently spherical caps, lines, and dumbbells of PCs can be obtained by inkjet printing (Figure 9.5b). The experimental and theoretical results demonstrate that surface tension difference of $0.77 - 1.50 \text{ mN m}^{-1}$ leads to the formation of straight lines due to the appropriate surface dynamic wettability to ink droplets [80].

9.2.2.3 Suppression of “Coffee-Ring” Effect

When a drop of liquid dries on a solid surface, its solutes prefer to deposit along the periphery, leaving a unique ring-like morphology. This phenomenon is known as “coffee-ring” effect. In fact, this phenomenon is named from our daily life. We always notice that when a drop of coffee splashes onto the table, a few dense rings along the edge of the small drops are left on the table. The dense rings tell us that there is much more coffee powder deposited at the edge. The “coffee-ring” effect is induced by the unsymmetrical evaporation during droplet drying. Not only coffee drops, other drops containing particles or solutes also leave similar rings on the substrate after drying. The “coffee-ring” effect is a universal phenomenon in nature.

However, it is very important to obtain films with uniform deposition for the application of printing, painting, inkjet printing, and so on. Improving the uniformity of deposited film can enhance the precision and resolution of patterns as well as improve the performance of fabricated functional devices [81]. Therefore, one of the key problems to enhance the resolution of patterns and the performance of the devices is how to eliminate the “coffee-ring” effect during the printing process. Over the past decades, numerous works have been devoted to understanding the formation mechanism as well as avoiding this inhomogeneous deposition. In 1997, Deegan *et al.* reported this phenomenon and carried out intensive investigations. They concluded that the peripheral ring deposition is induced by an outward radial capillary flow carrying particles toward the pinned TCL [82–84]. As shown in Figure 9.6, the evaporation flux is highest at the edge due to the wedge geometry, and the excess solvent lost at the edge must be replenished by solvent in the droplet center for a droplet with pinned TCL. As a result, the drawn solvent carries the solutes toward the TCL to form ring-shaped deposition after droplet drying. They pointed out that TCL pinning is one of the essential conditions for ring deposition. Adachi *et al.* investigated the evaporation process of droplets containing polystyrene spheres on hydrophilic glass surface [85]. They found that the stick-slip motion of TCL occurs during evaporation. When the TCL sticks on the surface, the spheres migrate to and deposit at the droplet edge. When the TCL slips on the surface, there is no sphere depositing. This oscillatory motion results in the formation of stripe patterns. Besides the pinning TCL, Marangoni flow within an evaporating droplet is another crucial factor of influencing the “coffee-ring” effect [86]. Marangoni flow is a kind of liquid convection independent of gravity, which was first reported by C. Marangoni in 1865. A liquid with a high surface tension pulls more strongly on the surrounding liquid

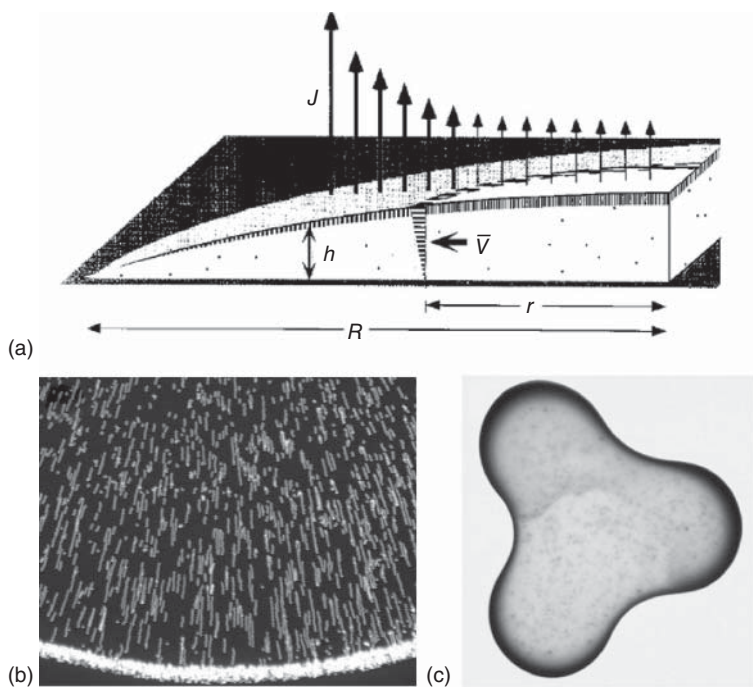


Figure 9.6 (a) Schematic illustration of the evaporative flux distribution of the droplet surface. (b) Particles migrating to the edge of the droplet during evaporation. (c) A ring-shaped deposition on substrate. (Deegan *et al.* (1997) [82]. Reproduced with permission of Nature Publishing.)

than one with a low surface tension. Therefore, when a gradient in surface tension presents, the liquid flows from regions of low surface tension to regions of high surface tension. This surface tension gradient can be caused by a concentration gradient or by a temperature gradient. Based on the mechanism, three strategies have been developed to suppress the “coffee-ring” effect, including (i) depinning the TCL, (ii) boosting the inward Marangoni flow, and (iii) restraining the outward capillary flow.

TCL pinning on surface is a common phenomenon for an evaporating droplet. It is caused by the chemical heterogeneity or rough structure on the surface or the solutes deposited on the substrate [82–84]. A depinned TCL could effectively avoid the “coffee-ring” effect since TCL pinning is an essential condition for the ring-shape deposition. Song *et al.* modified the substrates with high receding CA (θ_R) and allowed the TCL to freely slide on the substrates [43]. By controlling the sliding TCL of printed droplets, closely packed PC domes without “coffee-ring” effect were obtained. They found that the TCL pinned firmly on substrates with low θ_R and the particles deposited in a ring-like morphology. On substrates with high θ_R , the “coffee-ring” effect was suppressed, and a closely packed PC dome was formed. On such a substrate, the TCL continuously slides on the surface and pushes the particles moving inward. The driving force for impelling the particles

to move inward is derived from the sufficient superiority of a capillary force from TCL over an attractive force from substrate. Besides enhancing the θ_R of substrates, electrowetting method is also able to regulate the TCL behavior as well as the particle deposition [87]. By applying electrowetting with an alternating voltage on an evaporating droplet, the electrostatic force prevents TCL pinning and internal flow fields are generated to counteract the outward evaporation flow. Both these effects contribute to the suppression of ring-shaped deposition.

The TCL of printed droplets is usually pinned on the surface for most substrates. Since the capillary flow within the evaporating droplets is the key factor to the formation of ring-shaped deposition, restraining this flow is crucial for suppressing the “coffee-ring” effect. Jamming of particles on the liquid surface can retard this outward flow [88]. Yunker *et al.* obtained uniform deposition by simply using ellipsoidal particles or mixing small number of the ellipsoidal particles to spherical ones [89]. These ellipsoidal particles deform the air–water interfaces, producing strong interparticle capillary interaction. After the particles are carried to the air–water interface, loosely packed particle structures are formed due to the strong interaction, resulting in the increase of liquid viscosity, which restrains outward particle migration and ensures uniform deposition. Not only the ellipsoidal particles but other anisotropic particles such as rod-like, filament-like [89], and disk-like [90] particles have also been used to suppress the “coffee-ring” deposition. It is worth mentioning that the existence of surfactant will greatly reduce the interparticle capillary interaction, which results in the ellipsoidal particles moving more easily to the edge of droplet to form ring-like deposition. Besides employing anisotropic particles, increasing the viscosity of printing droplets by adding polymer monomers also effectively alters the capillary flow within the droplets and forming uniform deposition [41]. On one hand, the high viscosity induced by polymerization can reduce the migration rate of the particles to the edge of droplets and aids in the formation of uniform deposition with well-ordered assembly structure. On the other hand, the monomers would not polymerize during the printing process. Therefore, the inks are able to retain low viscosity and ensure the printing fluidity. Other methods, such as lowering the evaporation temperature [29], altering the pH value of inks [91], and guiding the evaporation by a mask upon the droplets [92], are also effective in controlling the capillary flow within the evaporating droplets and succeed in the suppression of “coffee-ring” effect.

Another strategy to suppress “coffee-ring” effect is to induce an additional inward Marangoni flow within an evaporating droplet. An effective method is to add solvent with higher boiling point and lower surface tension to the ink formulation [63, 81, 93, 94]. Ethylene glycol is a preferable choice in aqueous inks. When a portion of ethylene glycol is added, an additional surface tension gradient is produced by the concentration gradient of the solvent component between the center and edge of the droplet due to the different vaporizing rates of water and ethylene glycol. This additional surface tension gradient drives the fluid flow inward. It is reported that when the concentration of ethylene glycol reached 32 wt%, a uniform deposit of silver nanoparticles can be obtained. The Marangoni flow in an evaporating sessile droplet can be influenced significantly by surfactants as well [95]. As reported, the surfactants were able to create

localized swirling flows, termed as “Marangoni eddies” [96, 97]. These eddies reverse the outward capillary flow and prevent particle deposition at the drop perimeter. By adding a small amount of surfactant, a rather uniform deposition is obtained.

9.3 Application of Printing of Photonic Crystals

Inkjet printing is a very outstanding technique of quickly fabricating devices. Printed PCs have abundant applications in optical devices, displays, and microfluidic devices. In fact, versatile PC patterns can be facily obtained by inkjet printing. The brilliant structure color of PCs is widely utilized for information displays. The ability of responding to the external field based on the stopband shift and the band-edge-induced fluorescence enhancement effect allows PCs to serve as sensors. In the following sections, several typical applications of printed PCs are introduced.

9.3.1 Photonic Crystal Patterns

Fabrication of patterned PCs by a commercial inkjet printer affords an effective approach for designing functional devices. PC patterns consist of PC dots or lines, where the pattern can be designed by computer software. The brightness of the PC images is usually determined by the combined action of the reflection strength of single PC dots or lines and their effective coverage on the substrate. It is found that the better arrangement of particles can be obtained on substrates with higher contact angle. But the coverage will decrease on such substrates due to the less droplet-spreading area. As a result, substrates with appropriate contact angle should be employed for giving consideration to the spreading of ink droplets and the well-ordered assembly of particles, which contributes to the maximum brightness of printed PC patterns. Figure 9.7 shows the PC patterns with bright colors directly printed from a commercial printer by using latex suspensions with different diameters as printing inks [20]. The latex particles have hydrophobic polystyrene core and hydrophilic poly(methylmethacrylate) (PMMA)/polyacrylic acid (PAA) shell. The hydrophilic PAA shell with abundant $-\text{COOH}$ groups promotes the formation of hydrogen bonding interactions, which strengthen the linkage among latex particles and accelerates the assembly rate. The viscosity of the latex suspension is about 1 mPa.s, low enough for the fluent ejection of ink droplets. The surface tension of the latex suspension is about 57 mN m^{-1} , facilitating the spreading of ink droplets. The ink formulation contains a second solvent of ethylene glycol (40 wt%) to avoid the “coffee-ring” deposit pattern and obtain well-ordered assembly structure. The optimized water contact angle of the substrate is about 62° , ensuring the ink droplet spreading and particle assembly. All of these factors assist the fabrication of PC dots with homogenous deposit pattern, well-ordered assembly structure, and enough surface coverage. Patterns consisting of the PC dots printed in the aforementioned conditions exhibit brilliant colors, demonstrating good optical properties. The stopband and reflection color of printed PCs are regulated by

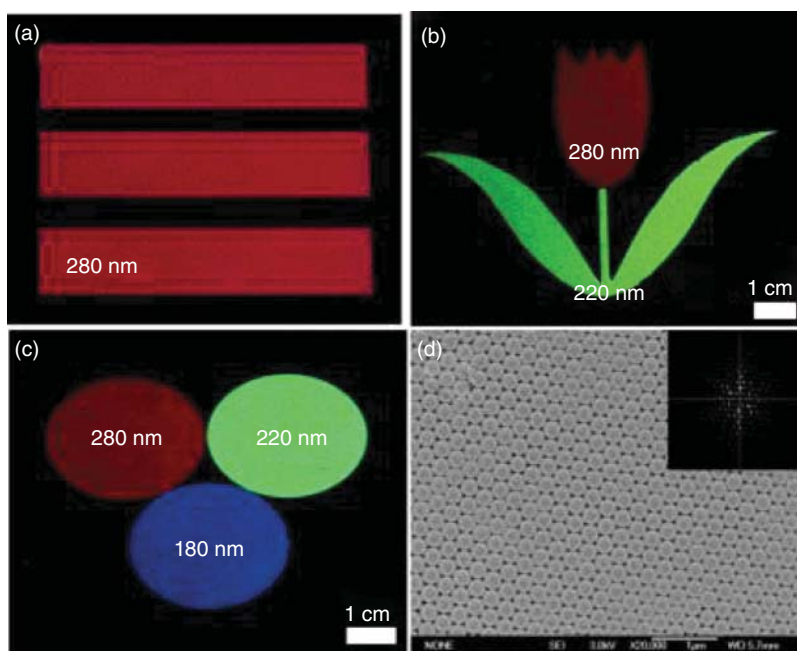


Figure 9.7 (a–c) Optical photos of inkjet-printed colloidal PC patterns. (d) SEM images of the printed PC dots. (Cui *et al.* (2009) [20]. Reproduced with permission of Royal Society of Chemistry.)

the diameter of the latex particles: the red, green, and blue areas are printed from particles with diameters of 280, 220, and 180 nm, respectively. The latex suspensions with varied particle diameters are held in different cartridges and printed from different nozzles. Filtration is needed for the latex suspensions before being injected into the cartridges in order to filter out the coagulants in the suspension, which will clog the printing nozzles. In addition, it is suggested that the particle diameter in the ink suspensions should not exceed 500 nm in order to avoid nozzle clogging.

According to the theory of Bragg diffraction, PCs present different structural colors when observed at varied angles [98]. In practical applications, the intrinsic angle-dependence character of PCs would restrain their performances in wide-viewing-angle displays. Many novel materials and assembly structures have been developed to achieve angle-independent PCs [99–105]. One of the strategies is to fabricate spherical PCs, on which the incident light is invariably perpendicular to the $\langle 111 \rangle$ plane of fcc lattice. However, it is difficult to obtain spherical PCs for the common vertical deposition method. Inkjet printing method has the facility to control the morphology of single PC dots by adjusting the wettability of substrates and the surface tension of the inks. It was introduced in the earlier section that the height–diameter ratio (H/D) and the assembly structure of printed PC dots can be tuned by varying the receding contact angle of the substrate. It is found that the H/D value increases from 0.00328 to 0.509

when the receding contact angle increases from $18.0 \pm 5.7^\circ$ to $93.3 \pm 1.9^\circ$ [43]. Meanwhile, the latex particles are arranged in a more closely packed manner on a substrate with higher receding contact angles. For the flat PC films, the stopbands of PC dots shift obviously as the detecting angle changes. With the increase in H/D ratio, the stopband variations with detecting angles become smaller. When it increases to 0.375, the printed PC dots reach a constant stopband, which shows a well-assembled hexagonal structure extending across the entire surface. This unique structure results in isotropic structure colors from 0° to 90° due to the incident light invariably being perpendicular to their $\langle 111 \rangle$ plane of fcc lattice. In addition, omnibearing fluorescent enhancement is realized on such spherical PC dots due to their isotropic stopband. The PC dots with an H/D ratio of 0.509 exhibit enhanced fluorescent intensity higher than 40 times owing to the large surface area and slow photon effect. The fluorescent PC dots also exhibit an excellent wide viewing angle from 0° to 180° benefited from the high H/D ratio (Figure 9.8a). These angle-independent PC dots can be printed to form versatile patterns on various substrates. This strategy is of great importance for the development of flexible, wide viewing angle displays and could provide an efficient strategy for fabricating advanced display and other optical devices. Instead of incorporating fluorescent molecules into the printing inks, reactive inkjet printing inks that fabricate semiconductor quantum dots containing PC nanocomposites are designed to generate PC patterns with high fluorescent display (Figure 9.8b)[44]. Cadmium sulfide (CdS) quantum dots are synthesized in situ during the particle assembly process. After the particle assembles into a well-ordered arrangement, CdS quantum dots are homogenously distributed between the intervals of the particles. Fluorescent quantum dots containing

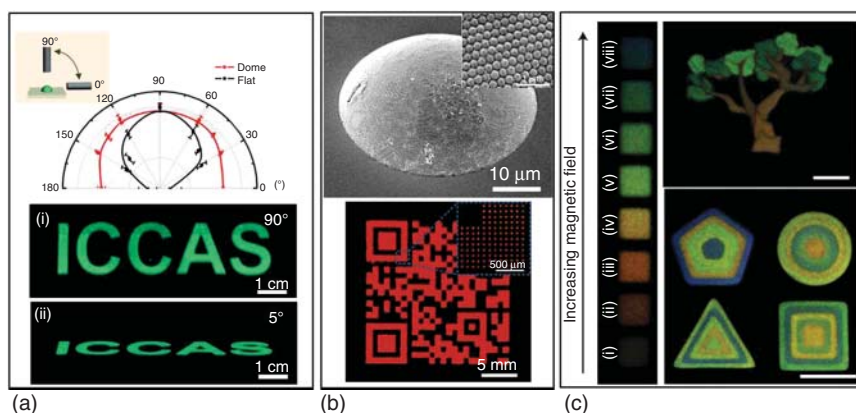


Figure 9.8 (a) The fluorescent PC domes exhibit an excellent wide viewing angle from 0° to 180° . PC patterns consisting of fluorescent PC domes display consistent strong fluorescent images of either top view or side view. (Kuang *et al.* (2014) [43]. Reproduced with permission of Wiley.) (b) SEM images of a single PC dome printed by reactive inks and the fluorescent image of a PC dot-matrix-constructed 2D code pattern. (Bao *et al.* (2015) [44]. Reproduced with permission of Wiley.) (c) Optical images of various PC patterns obtained by magnetic screen printing. Scale bar: $100 \mu\text{m}$. (Kim *et al.* (2009) [106]. Reproduced with permission of Nature Publishing.)

nanocomposite patterns are of significance in high-efficiency luminescent devices, anticounterfeiting technology, and other applications.

PC patterns with variable colors are obtained by applying responsive latex particles or incorporating responsive materials. These PC patterns show different structure colors under varied exterior environment, such as magnetic field [9, 107, 108], electrical field [109], light, and humidity [110–114]. For example, patterned PCs are fabricated by screen printing, where the magnetic latex particles are assembled into ordered structures under the magnetic force (Figure 9.8c) [106]. And the magnitude of applied magnetic force controls the interval space between particles, which determines the reflection color of PCs. By regional photocuring the particle assembly structure individually, PC patterns with versatile colors are facilely obtained.

9.3.2 Printing Patterned Microcolloidal Crystals with Controllable 3D Morphology

The printing substrate is not homogeneous in some special cases. It is designed to have surface energy patterns. Ink droplets printed on such substrates adapt certain morphology depending on the surface patterns and the characteristics of the droplets, such as volume and surface tension [115]. When the dimension of printed droplets is roughly the size of hydrophilic area, the droplets exactly locate on the hydrophilic zone and form patterns identical to the hydrophilic pattern on the surface. The baseline of these droplets copies the hydrophilic outline [115]. But when a droplet has a volume larger than the size of hydrophilic area, it may crossover two or more hydrophilic zones and adapt deformed shapes. As shown in Figure 9.9, 3D PC dot arrays with various shapes are inkjet printed on surface-energy-patterned substrates [116]. The hydrophilic patterns determine the shapes of fabricated PC dots due to the axisymmetric TCL retraction on such substrates. During the evaporation process, the TCL pins on hydrophilic zone and retracts on hydrophobic zone. This axisymmetric TCL retraction guides particle assembly and the shape of obtained PCs. In a typical particle assembly process, TCL first retracts uniformly inward toward the hydrophobic region. Then, the hydrophilic points with high surface energy serve as pinning points to confine this shrinking process subsequently. As a result, TCL pins on the periphery of the hydrophilic points on substrates with spaced pinning points. With further retracting of TCL on the surface, asymmetric retracting of TCL occurs, which leads to the formation of liquid droplets with controllable 3D morphology. At the same time, the colloidal particles move with the TCL and assemble along the curved surface of the droplet, which finally form PCs with 3D structures.

The final morphology of the colloidal crystals formed on such patterned surfaces can be deduced by balancing the relative acting ingredients as $F_{\Delta RCA}$ equals $F_{\text{resistance}}$, which are related to liquid properties, such as surface tension and particle concentration, and the pinning pattern parameters including pinning points' geometrical shape, distance, arrangement, and wetting property.

$$F_{\Delta RCA} = \Delta l_1 \gamma \cos \theta_{R1} - \Delta l_2 \gamma \cos \theta_{R2} \quad (9.2)$$

where γ is the surface tension of the dispersion; θ_{R1} and θ_{R2} are the receding contact angles of dispersion on the hydrophilic and hydrophobic regions,

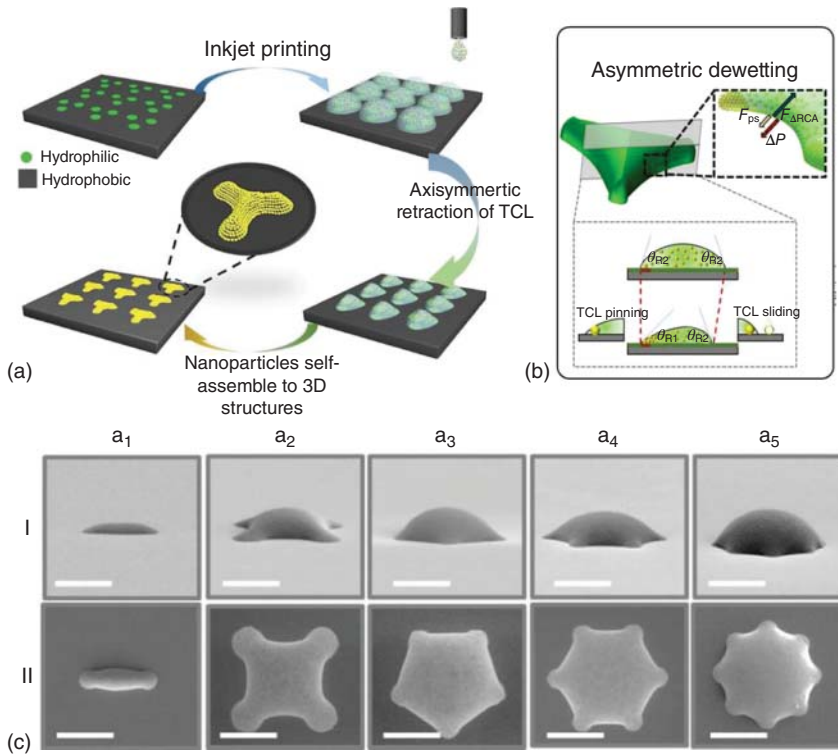


Figure 9.9 (a) Schematic illustration of manipulating 3D morphology of microcolloidal PC pattern through hydrophilic pattern-induced asymmetric dewetting. (b) Mechanism of pinning points induced asymmetric dewetting and assembly. (c) SEM images of controllable 3D structures include line a_1 , quadrilateral a_2 , star a_3 , hexagonal a_4 , and octagon a_5 . Scale bar: 20 μm. (Wu *et al.* (2015) [116]. Reproduced with permission of Wiley.)

respectively; and Δl_1 and Δl_2 are effective lengths of different wettabilities.

$$F_{\text{resistance}} = A\Delta P + F_{\text{PS}} = A \int_{w_2}^{w_1} \gamma \left(\frac{1}{r} + \frac{1}{R} \right) dw + 6\pi R_{\text{PS}} \sqrt{\frac{G^*}{E^*}} \Delta\gamma \quad (9.3)$$

where A is the contact area on the substrate; w is the width of the liquid film; w_1 and w_2 are the stopping and starting positions of TCL, respectively; r and R are the local radii, which are influenced by w ; R_{PS} is the radius of nanoparticle; and G^* , E^* , or $\Delta\gamma$ is the average shear modulus, average Young's modulus, or average surface energy of particle and substrate, respectively.

In detail, the printed ink droplet with a higher surface tension possesses a larger driving force $F_{\Delta RCA}$ according to Equation 9.2. The larger driving force leads to a larger retracting distance and a more stereoscopic morphology. Meanwhile, increasing the particle concentration leads to a larger width and height of the 3D structures due to the larger $F_{\text{resistance}}$ according to Equation 9.3. Besides liquid properties, the diverse 3D morphology can also be regulated by varying the pinning patterns. Increasing surface energy difference of the heterowettable substrate, a more stereoscopic morphology can be achieved.

These printed 3D PC arrays display bright structure color. Due to the diverse morphology and the distribution of the 3D PC microdots, multi-information carrier or anticounterfeiting materials can be fabricated based on the macro/microhierarchical structure color patterns.

9.3.3 Inkjet-Printed PCs Applied in Vapor Sensors

In nature, some beetles such as *Dynastes hercules* and *Longhorn* beetles are able to respond to environment humidity by changing their colors. For example, the elytra of the *D. hercules* appear green in a dry atmosphere and turn into black in an environment with high humidity [117]. This change in color is attributed to the three-dimensional photonic crystal structures under the cuticle surface of elytra. After the elytra are swelled by water vapor, the change in refractive index with respect to the humidity level induces the variation in the visible color. Inspired by the humidity-sensing behavior of beetles, many artificial vapor-sensitive colloidal PCs are fabricated. Song *et al.* fabricated a colorful humidity-sensitive PC hydrogel by infiltrating hydrophilic polyacrylamide (PAAm) solution into the interstice of the opal template [114]. When the humidity increases or decreases, the PAAm swells or deswells, resulting in changes of the colloid interval. The color of the samples is able to reversibly vary from transparent to violet, blue, cyan, green, and red according to the humidity conditions. The hydrophilicity of PCs is responsible for the quick diffusion of the water vapor into the PC film, contributing to the quick sensing of the humidity change.

Inkjet printing technique has superior performance in fabricating microsensor arrays. With the increasing demand of quick sensing, a PC device with a fast response rate is highly desired. In order to increase the response rate of PCs, Song *et al.* took advantage of the combined effects of intrinsic small size of the inkjet microdots and the hydrophobic transition of poly(*N*-isopropyl acrylamide) (PNIPAm) (Figure 9.10) [41]. The printed PC microdots have dimensions of 20–30 μm , which is much smaller than general PCs with dimensions of hundreds of micrometers. The tiny volume contributes to the rapid response. Another factor contributing to the fast response rate is the introduction of PNIPAm segments into the PC microdots. The reversible phase transition of PNIPAm modulates the wetting states of adsorbed water on the polymer segments from Wenzel state to Cassie state, resulting in the remarkable improvement of response rate. A fast response rate of 1.2 s in swelling process and 1.8 s in deswelling process are successfully achieved when the PC microdots are alternately exposed to water vapor. Besides water vapor, other vapor PC sensors such as ethanol sensor are inkjet printed by incorporating functional materials into the printing inks [118]. The reflection color could quickly change when the vapor content of the environment changes.

9.3.4 Inkjet-Printed PCs Applied in Chemical Detection

Analyte detection has important applications in early diagnosis [119], explosives detection [120], drugs testing [121], contamination detection [122], and so on. Designing sensitive and effective sensors has attracted enormous interest over

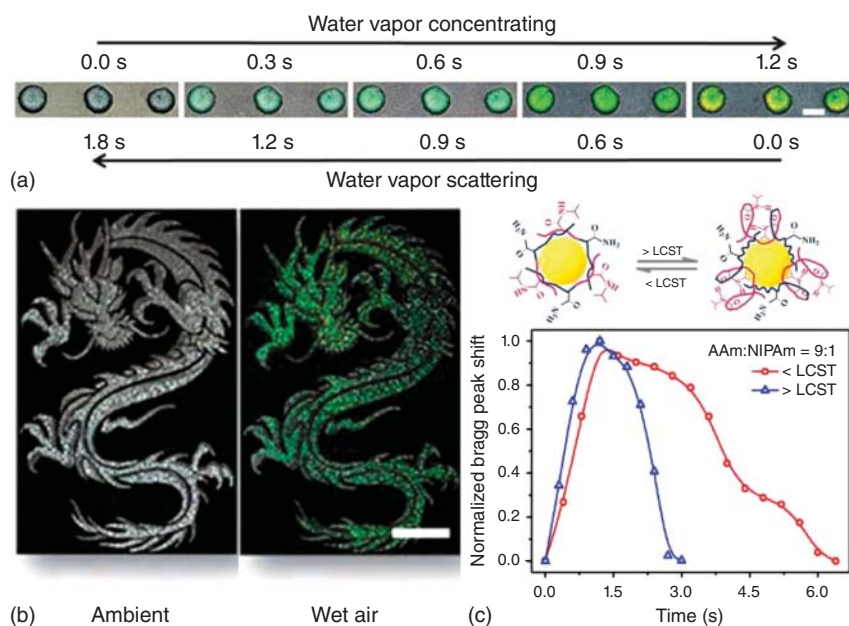


Figure 9.10 (a) Real-time optical microscope images of the colloidal PC microdots as water vapor is concentrating and scattering. Scale bar: 20 μm . (b) Color photographs of dragon images taken in low (left) and high (right) concentration of wet air. Scale bar: 5 mm. (c) Top: hydrophobic transition of the molecular conformation of PAAm-co-PNIPAm incorporated in the PC microdot. Bottom: changes of the Bragg diffraction peak shift of PC microdots with response time. (Wang *et al.* (2012) [41]. Reproduced with permission of Royal Society of Chemistry.)

the past years [123–125]. PC films have been demonstrated to have sensing ability for ions [8, 18, 126, 127], DNA [128, 129], proteins [19, 129–131], and other molecules [132–136]. A fast and handy detector is one of the development trends of analyte detection. Inkjet printing is a very outstanding technique of quickly fabricating devices. Printed PCs are widely used in constructing detection sensors.

Inkjet printing technique has a merit of fabricating devices on various substrates. Taking advantage of this character, a hydrophilic PC sensor can be designed on a hydrophobic substrate, which is beneficial for guiding the flow of detecting liquid based on the surface energy discrepancy. Figure 9.11a shows a Y-shaped PC microfluidic immune assay constructed by inkjet printing technique [40]. The hydrophilic PC pattern on the superhydrophobic substrate serves as a surface-tension confined microfluidic channel for guiding the fluidic transport. The detecting liquid flows along the PC channels from the head of injection spot to the ends of the two branches with and without the antibody probe. Utilizing this chip, a prototype human IgG antigen–antibody colorimetric detection is realized based on the responsive wavelength shift of photonic stopband. Figure 9.11b shows a highly sensitive PC microchip based on hydrophilic–hydrophobic micropattern fabricated by inkjet printing. Scientists

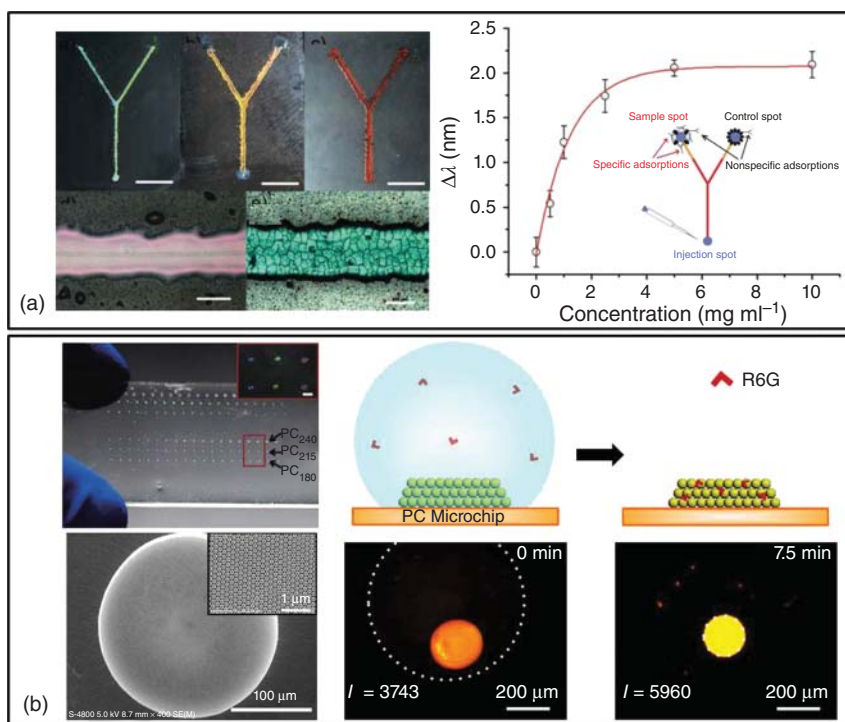


Figure 9.11 (a) Digital photographs and micrographs of inkjet-printed PC chips. Scale bar: 5 mm. The normalized detection results ($\Delta\lambda$) computed from differences between the sample spot and control spot data. (Shen *et al.* (2012) [40]. Reproduced with permission. Copyright 2012 The Royal Society of Chemistry). (b) PC microchip with hydrophilic PC dots on hydrophobic substrate. The wettability difference in water CA between the hydrophilic PC dot and hydrophobic substrate induces the target molecules to enrich the active PC microsensors. (Hou *et al.* (2014) [137]. Reproduced with permission of Wiley.)

mimic the fog-collecting ability of *Stenocara* beetles, which live in extremely arid deserts, which automatically aggregate droplets to the hydrophilic area on their back. As shown in Figure 9.11b, the contact angle of the printed PC dots is $46.4 \pm 3.48^\circ$, whereas the contact angle of the substrate is $115.0 \pm 3.18^\circ$. When a detecting droplet evaporates on the surface, its TCL pins on hydrophilic PC dot but recedes on hydrophobic substrate. Under the behavior of this directional TCL sliding, the analytes are enriched into the PC dots gradually to enhance their concentration. Coupled with the fluorescence enhancement effect of the PCs, detection down to $10^{-16} \text{ mol l}^{-1}$ is achieved [137].

9.4 Outlook

Inkjet printing of PCs has become increasingly important in fabricating functional optical devices. Although tremendous research works on inkjet printing of

PCs have been reported, the fabrication and applications of PC patterns with special functionality still remain as challenges. First, the fabrication of continuous, high-resolution, and multifunctional PC devices is desired. Second, the applications of patterned PCs are still in the early stages. Fabricating high-performance PC patterns is required for constructing advanced optical devices. Third, interdisciplinary researches are demanded to develop the fabrication and applications of novel and advanced functional PC patterns by chemists, physicists, materials scientists, engineers, and biologists. It is anticipated that the development of inkjet printing of PCs will greatly broaden the applications of PCs in various optical devices.

References

- 1 von Freymann, G., Kitaev, V., Lotsch, B.V., and Ozin, G.A. (2013) Bottom-up assembly of photonic crystals. *Chem. Soc. Rev.*, **42**, 2528–2554.
- 2 MacLeod, J. and Rosei, F. (2013) Photonic crystals: Sustainable sensors from silk. *Nat. Mater.*, **12**, 98–100.
- 3 Kondo, K. *et al.* (2013) Ultrafast slow-light tuning beyond the carrier lifetime using photonic crystal waveguides. *Phys. Rev. Lett.*, **110**, 053902.
- 4 Kaji, T. *et al.* (2013) Controlled spontaneous emission of single molecules in a two-dimensional photonic band gap. *J. Am. Chem. Soc.*, **135**, 106–109.
- 5 Zhang, Y.Q., Huang, Y.G., Parrish, D.A., and Shreeve, J.M. (2011) 4-Amino-3,5-dinitropyrazolate salts-highly insensitive energetic materials. *J. Mater. Chem.*, **21**, 6891–6897.
- 6 Arpin, K.A. *et al.* (2010) Multidimensional architectures for functional optical devices. *Adv. Mater.*, **22**, 1084–1101.
- 7 Burgess, I.B. *et al.* (2011) Encoding complex wettability patterns in chemically functionalized 3D photonic crystals. *J. Am. Chem. Soc.*, **133**, 12430–12432.
- 8 Ge, J.P., Goebl, J., He, L., Lu, Z.D., and Yin, Y.D. (2009) Rewritable photonic paper with hygroscopic salt solution as ink. *Adv. Mater.*, **21**, 4259–4264.
- 9 Ge, J.P. and Yin, Y.D. (2011) Responsive photonic crystals. *Angew. Chem., Int. Ed.*, **50**, 1492–1522.
- 10 Zhang, Y.Z. *et al.* (2008) Photonic crystal concentrator for efficient output of dye-sensitized solar cells. *J. Mater. Chem.*, **18**, 2650–2652.
- 11 Wang, Z.H. *et al.* (2010) Bioinspired water-vapor-responsive organic/inorganic hybrid one-dimensional photonic crystals with tunable full-color stop band. *Adv. Funct. Mater.*, **20**, 3784–3790.
- 12 Cui, L.Y., Song, Y.L. *et al.* (2010) Enhanced sensitivity in a Hg²⁺ sensor by photonic crystals. *Anal. Methods*, **2**, 448–450.
- 13 Tian, E.T., Cui, L.Y., Wang, J.X., Song, Y.L., and Jiang, L. (2009) Tough photonic crystals fabricated by photo-crosslinkage of latex spheres. *Macromol. Rapid Commun.*, **30**, 509–514.
- 14 Tian, E.T., Song, Y.L. *et al.* (2009) Color-oscillating photonic crystal hydrogel. *Macromol. Rapid Commun.*, **30**, 1719–1724.

- 15 Zhang, J.H. and Yang, B. (2010) Patterning colloidal crystals and nanostructure arrays by soft lithography. *Adv. Funct. Mater.*, **20**, 3411–3424.
- 16 He, L., Wang, M.S., Ge, J.P., and Yin, Y.D. (2012) Magnetic assembly route to colloidal responsive photonic nanostructures. *Acc. Chem. Res.*, **45**, 1431–1440.
- 17 Xuan, R.Y. and Ge, J.P. (2012) Invisible photonic prints shown by water. *J. Mater. Chem.*, **22**, 367–372.
- 18 Huang, Y., Li, F.Y., Qin, M., Jiang, L., and Song, Y.L. (2013) A multi-stopband photonic-crystal microchip for high-performance metal-ion recognition based on fluorescent detection. *Angew. Chem., Int. Ed.*, **52**, 7296–7299.
- 19 Zhao, Y.J., Zhao, X.W., and Gu, Z.Z. (2010) Photonic crystals in bioassays. *Adv. Funct. Mater.*, **20**, 2970–2988.
- 20 Cui, L.Y., Song, Y.L. *et al.* (2009) Fabrication of large-area patterned photonic crystals by ink-jet printing. *J. Mater. Chem.*, **19**, 5499–5502.
- 21 Kang, P.G., Ogunbo, S.O., and Erickson, D. (2011) High resolution reversible color images on photonic crystal substrates. *Langmuir*, **27**, 9676–9680.
- 22 Cui, L.Y., Song, Y.L. *et al.* (2009) Ultra-fast fabrication of colloidal photonic crystals by spray coating. *Macromol. Rapid Commun.*, **30**, 598–603.
- 23 Sirringhaus, H. *et al.* (2000) High-resolution inkjet printing of all-polymer transistor circuits. *Science*, **290**, 2123–2126.
- 24 Wang, J.Z., Zheng, Z.H., Li, H.W., Huck, W.T.S., and Sirringhaus, H. (2004) Dewetting of conducting polymer inkjet droplets on patterned surfaces. *Nat. Mater.*, **3**, 171–176.
- 25 Sele, C.W., von Werne, T., Friend, R.H., and Sirringhaus, H. (2005) Lithography-free, self-aligned inkjet printing with sub-hundred-nanometer resolution. *Adv. Mater.*, **17**, 997–1001.
- 26 Jang, J., Ha, J., and Cho, J. (2007) Fabrication of water-dispersible polyaniline-poly(4-styrenesulfonate) nanoparticles for inkjet-printed chemical-sensor applications. *Adv. Mater.*, **19**, 1772–1775.
- 27 Abe, K., Suzuki, K., and Citterio, D. (2008) Inkjet-printed microfluidic multi-analyte chemical sensing paper. *Anal. Chem.*, **80**, 6928–6934.
- 28 Hendriks, C.E., Smith, P.J., Perelaer, J., Van den Berg, A.M.J., and Schubert, U.S. (2008) "Invisible" silver tracks produced by combining hot-embossing and inkjet printing. *Adv. Funct. Mater.*, **18**, 1031–1038.
- 29 Soltman, D. and Subramanian, V. (2008) Inkjet-printed line morphologies and temperature control of the coffee ring effect. *Langmuir*, **24**, 2224–2231.
- 30 Tekin, E., Smith, P.J., and Schubert, U.S. (2008) Inkjet printing as a deposition and patterning tool for polymers and inorganic particles. *Soft Matter*, **4**, 703–713.
- 31 van Osch, T.H.J., Perelaer, J., de Laat, A.W.M., and Schubert, U.S. (2008) Inkjet printing of narrow conductive tracks on untreated polymeric substrates. *Adv. Mater.*, **20**, 343–345.
- 32 Singh, M., Haverinen, H.M., Dhagat, P., and Jabbour, G.E. (2010) Inkjet printing-process and its applications. *Adv. Mater.*, **22**, 673–685.
- 33 Kirk, J.T. *et al.* (2011) Multiplexed inkjet functionalization of silicon photonic biosensors. *Lab Chip*, **11**, 1372–1377.

- 34 Marjanovic, N. *et al.* (2011) Inkjet printing and low temperature sintering of CuO and CdS as functional electronic layers and Schottky diodes. *J. Mater. Chem.*, **21**, 13634–13639.
- 35 Minemawari, H. *et al.* (2011) Inkjet printing of single-crystal films. *Nature*, **475**, 364–367.
- 36 Zhang, L. *et al.* (2012) Inkjet printing high-resolution, large-area graphene patterns by coffee-ring lithography. *Adv. Mater.*, **24**, 436–440.
- 37 Zhang, Z.L. *et al.* (2013) Controlled inkjetting of a conductive pattern of silver nanoparticles based on the coffee-ring effect. *Adv. Mater.*, **25**, 6714–6718.
- 38 Li, L.H., Guo, Y.Z., Zhang, X.Y., and Song, Y.L. (2014) Inkjet-printed highly conductive transparent patterns with water based Ag-doped graphene. *J. Mater. Chem. A*, **2**, 19095–19101.
- 39 Yang, Q., Song, Y.L. *et al.* (2015) Highly reproducible SERS arrays directly written by inkjet printing. *Nanoscale*, **7**, 421–425.
- 40 Shen, W.Z., Li, M.Z., Ye, C.Q., Jiang, L., and Song, Y.L. (2012) Direct-writing colloidal photonic crystal microfluidic chips by inkjet printing for label-free protein detection. *Lab Chip*, **12**, 3089–3095.
- 41 Wang, L.B., Song, Y.L. *et al.* (2012) Inkjet printed colloidal photonic crystal microdot with fast response induced by hydrophobic transition of poly(N-isopropyl acrylamide). *J. Mater. Chem.*, **22**, 21405–21411.
- 42 Wang, J.X., Wang, L.B., Song, Y.L., and Jiang, L. (2013) Patterned photonic crystals fabricated by inkjet printing. *J. Mater. Chem. C*, **1**, 6048–6058.
- 43 Kuang, M.X., Song, Y.L. *et al.* (2014) Inkjet printing patterned photonic crystal domes for wide viewing-angle displays by controlling the sliding three phase contact line. *Adv. Opt. Mater.*, **2**, 34–38.
- 44 Bao, B., Song, Y.L. *et al.* (2015) Patterning fluorescent quantum dot nanocomposites by reactive inkjet printing. *Small*, **11**, 1649–1654.
- 45 Chen, P.H., Chen, W.C., Ding, P.P., and Chang, S.H. (1998) Droplet formation of a thermal sideshooter inkjet printhead. *Int. J. Heat Fluid Flow*, **19**, 382–390.
- 46 Wijshoff, H. (2010) The dynamics of the piezo inkjet printhead operation. *Phys. Rep.*, **491**, 77–177.
- 47 Le, H.P. (1998) Progress and trends in ink-jet printing technology. *J. Imaging Sci. Technol.*, **42**, 49–62.
- 48 Derby, B. (2010) Inkjet printing of functional and structural materials: Fluid property requirements, feature stability, and resolution. *Annu. Rev. Mater. Res.*, **40**, 395–414.
- 49 Okumura, K., Chevy, F., Richard, D., Quere, D., and Clanet, C. (2003) Water spring: A model for bouncing drops. *Europhys. Lett.*, **62**, 237–243.
- 50 Clanet, C., Beguin, C., Richard, D., and Quere, D. (2004) Maximal deformation of an impacting drop. *J. Fluid Mech.*, **517**, 199–208.
- 51 Attane, P., Girard, F., and Morin, V. (2007) An energy balance approach of the dynamics of drop impact on a solid surface. *Phys. Fluids*, **19**, 2408495.
- 52 Chandra, S. and Avedisian, C.T. (1991) On the collision of a droplet with a solid-surface. *Proc. R. Soc. London, Ser. A*, **432**, 13–41.

- 53 Richard, D. and Quere, D. (2000) Bouncing water drops. *Europhys. Lett.*, **50**, 769–775.
- 54 Stow, C.D. and Hadfield, M.G. (1981) An experimental investigation of fluid-flow resulting from the impact of a water drop with an unyielding dry surface. *Proc. R. Soc. London, Ser. A*, **373**, 419–441.
- 55 Mundo, C., Sommerfeld, M., and Tropea, C. (1995) Droplet-wall collisions – experimental studies of the deformation and breakup process. *Int. J. Multiphase Flow*, **21**, 151–173.
- 56 Range, K. and Feuillebois, F. (1998) Influence of surface roughness on liquid drop impact. *J. Colloid Interface Sci.*, **203**, 16–30.
- 57 Range, K. and Feuillebois, F. (1998) Splashing of a drop on a rough surface. *High Temp. Mater. Processes*, **2**, 287–300.
- 58 Wang, J.X., Wen, Y.Q., Feng, X.J., Song, Y.L., and Jiang, L. (2006) Control over the wettability of colloidal crystal films by assembly temperature. *Macromol. Rapid Commun.*, **27**, 188–192.
- 59 Wang, J.X. *et al.* (2006) Simple fabrication of full color colloidal crystal films with tough mechanical strength. *Macromol. Chem. Phys.*, **207**, 596–604.
- 60 Chen, M., Wu, L.M., Zhou, S.X., and You, B. (2006) A method for the fabrication of monodisperse hollow silica spheres. *Adv. Mater.*, **18**, 801–806.
- 61 Qi, G.G. *et al.* (2010) Facile and scalable synthesis of monodispersed spherical capsules with a mesoporous shell. *Chem. Mater.*, **22**, 2693–2695.
- 62 Pell, L.E., Schricker, A.D., Mikulec, F.V., and Korgel, B.A. (2004) Synthesis of amorphous silicon colloids by trisilane thermolysis in high temperature supercritical solvents. *Langmuir*, **20**, 6546–6548.
- 63 Park, J. and Moon, J. (2006) Control of colloidal particle deposit patterns within picoliter droplets ejected by ink-jet printing. *Langmuir*, **22**, 3506–3513.
- 64 Zhou, J.M. *et al.* (2012) Large-area crack-free single-crystal photonic crystals via combined effects of polymerization-assisted assembly and flexible substrate. *NPG Asia Mater.*, **4**, 38.
- 65 Liu, K.S., Tian, Y., and Jiang, L. (2013) Bio-inspired superoleophobic and smart materials: Design, fabrication, and application. *Prog. Mater. Sci.*, **58**, 503–564.
- 66 Sun, T.L., Feng, L., Gao, X.F., and Jiang, L. (2005) Bioinspired surfaces with special wettability. *Acc. Chem. Res.*, **38**, 644–652.
- 67 Liu, K.S., Yao, X., and Jiang, L. (2010) Recent developments in bio-inspired special wettability. *Chem. Soc. Rev.*, **39**, 3240–3255.
- 68 Wong, T.S. *et al.* (2011) Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. *Nature*, **477**, 443–447.
- 69 Feng, X.J. and Jiang, L. (2006) Design and creation of superwetting/antiwetting surfaces. *Adv. Mater.*, **18**, 3063–3078.
- 70 Xia, F. and Jiang, L. (2008) Bio-inspired, smart, multiscale interfacial materials. *Adv. Mater.*, **20**, 2842–2858.
- 71 Ko, H.Y., Park, J., Shin, H., and Moon, J. (2004) Rapid self-assembly of monodisperse colloidal spheres in an ink-jet printed droplet. *Chem. Mater.*, **16**, 4212–4215.

- 72 Cui, L.Y. *et al.* (2012) Avoiding coffee ring structure based on hydrophobic silicon pillar arrays during single-drop evaporation. *Soft Matter*, **8**, 10448–10456.
- 73 Nguyen, T.A.H. and Nguyen, A.V. (2012) On the lifetime of evaporating sessile droplets. *Langmuir*, **28**, 1924–1930.
- 74 Shanahan, M.E.R., Sefiane, K., and Moffat, J.R. (2011) Dependence of volatile droplet lifetime on the hydrophobicity of the substrate. *Langmuir*, **27**, 4572–4577.
- 75 Huang, Y. *et al.* (2012) Colloidal photonic crystals with narrow stopbands assembled from low-adhesive superhydrophobic substrates. *J. Am. Chem. Soc.*, **134**, 17053–17058.
- 76 Kulinich, S.A. and Farzaneh, M. (2009) Effect of contact angle hysteresis on water droplet evaporation from super-hydrophobic surfaces. *Appl. Surf. Sci.*, **255**, 4056–4060.
- 77 Karpitschka, S. and Riegler, H. (2012) Noncoalescence of sessile drops from different but miscible liquids: Hydrodynamic analysis of the twin drop contour as a self-stabilizing traveling wave. *Phys. Rev. Lett.*, **109**, 066103.
- 78 Subramaniam, A.B., Abkarian, M., Mahadevan, L., and Stone, H.A. (2005) Non-spherical bubbles. *Nature*, **438**, 930.
- 79 Chen, G. *et al.* (2013) Coalescence of pickering emulsion droplets induced by an electric field. *Phys. Rev. Lett.*, **110**, 064502.
- 80 Liu, M.J. *et al.* (2014) Inkjet printing controllable footprint lines by regulating the dynamic wettability of coalescing ink droplets. *ACS Appl. Mater. Interfaces*, **6**, 13344–13348.
- 81 Kim, D., Jeong, S., Park, B.K., and Moon, J. (2006) Direct writing of silver conductive patterns: Improvement of film morphology and conductance by controlling solvent compositions. *Appl. Phys. Lett.*, **89**, 2424671.
- 82 Deegan, R.D. *et al.* (1997) Capillary flow as the cause of ring stains from dried liquid drops. *Nature*, **389**, 827–829.
- 83 Deegan, R.D. *et al.* (2000) Contact line deposits in an evaporating drop. *Phys. Rev. E*, **62**, 756–765.
- 84 Deegan, R.D. (2000) Pattern formation in drying drops. *Phys. Rev. E*, **61**, 475–485.
- 85 Adachi, E., Dimitrov, A.S., and Nagayama, K. (1995) Stripe patterns formed on a glass-surface during droplet evaporation. *Langmuir*, **11**, 1057–1060.
- 86 Hu, H. and Larson, R.G. (2006) Marangoni effect reverses coffee-ring depositions. *J. Phys. Chem. B*, **110**, 7090–7094.
- 87 Eral, H.B., Augustine, D.M., Duits, M.H.G., and Mugele, F. (2011) Suppressing the coffee stain effect: How to control colloidal self-assembly in evaporating drops using electrowetting. *Soft Matter*, **7**, 4954–4958.
- 88 Bigioni, T.P. *et al.* (2006) Kinetically driven self assembly of highly ordered nanoparticle monolayers. *Nat. Mater.*, **5**, 265–270.
- 89 Yunker, P.J., Still, T., Lohr, M.A., and Yodh, A.G. (2011) Suppression of the coffee-ring effect by shape-dependent capillary interactions. *Nature*, **476**, 308–311.

- 90 Hodges, C.S., Ding, Y., and Biggs, S. (2010) The influence of nanoparticle shape on the drying of colloidal suspensions. *J. Colloid Interface Sci.*, **352**, 99–106.
- 91 Bhardwaj, R., Fang, X.H., Somasundaran, P., and Attinger, D. (2010) Self-assembly of colloidal particles from evaporating droplets: Role of DLVO interactions and proposition of a phase diagram. *Langmuir*, **26**, 7833–7842.
- 92 Harris, D.J., Hu, H., Conrad, J.C., and Lewis, J.A. (2007) Patterning colloidal films via evaporative lithography. *Phys. Rev. Lett.*, **98**, 148301.
- 93 de Gans, B.J. and Schubert, U.S. (2004) Inkjet printing of well-defined polymer dots and arrays. *Langmuir*, **20**, 7789–7793.
- 94 Tekin, E., de Gans, B.J., and Schubert, U.S. (2004) Ink-jet printing of polymers – from single dots to thin film libraries. *J. Mater. Chem.*, **14**, 2627–2632.
- 95 Hu, H. and Larson, R.G. (2005) Analysis of the effects of Marangoni stresses on the microflow in an evaporating sessile droplet. *Langmuir*, **21**, 3972–3980.
- 96 Still, T., Yunker, P.J., and Yodh, A.G. (2012) Surfactant-induced Marangoni eddies alter the coffee-rings of evaporating colloidal drops. *Langmuir*, **28**, 4984–4988.
- 97 Sempels, W., De Dier, R., Mizuno, H., Hofkens, J., and Vermant, J. (2013) Auto-production of biosurfactants reverses the coffee ring effect in a bacterial system. *Nat. Commun.*, **4**, 1757.
- 98 Richel, A., Johnson, N.P., and McComb, D.W. (2000) Observation of Bragg reflection in photonic crystals synthesized from air spheres in a titania matrix. *Appl. Phys. Lett.*, **76**, 1816–1818.
- 99 Takeoka, Y. (2012) Angle-independent structural coloured amorphous arrays. *J. Mater. Chem.*, **22**, 23299–23309.
- 100 Chung, K. *et al.* (2012) Flexible, angle-independent, structural color reflectors inspired by morpho butterfly wings. *Adv. Mater.*, **24**, 2375–2379.
- 101 Lee, I. *et al.* (2010) Quasi-amorphous colloidal structures for electrically tunable full-color photonic pixels with angle-independency. *Adv. Mater.*, **22**, 4973–4977.
- 102 Kim, S.H., Jeon, S.J., and Yang, S.M. (2008) Optofluidic encapsulation of crystalline colloidal arrays into spherical membrane. *J. Am. Chem. Soc.*, **130**, 6040–6046.
- 103 Kim, S.H., Jeon, S.J., Jeong, W.C., Park, H.S., and Yang, S.M. (2008) Optofluidic synthesis of electroresponsive photonic janus balls with isotropic structural colors. *Adv. Mater.*, **20**, 4129–4134.
- 104 Gu, H.C. *et al.* (2013) Tailoring colloidal photonic crystals with wide viewing angles. *Small*, **9**, 2266–2271.
- 105 Ye, B.F. *et al.* (2013) Bioinspired angle-independent photonic crystal colorimetric sensing. *Chem. Commun.*, **49**, 5331–5333.
- 106 Kim, H. *et al.* (2009) Structural colour printing using a magnetically tunable and lithographically fixable photonic crystal. *Nat. Photonics*, **3**, 534–540.
- 107 Xuan, R.Y., Wu, Q.S., Yin, Y.D., and Ge, J.P. (2011) Magnetically assembled photonic crystal film for humidity sensing. *J. Mater. Chem.*, **21**, 3672–3676.

- 108 Hu, Y.X., He, L., and Yin, Y.D. (2011) Magnetically responsive photonic nanochains. *Angew. Chem., Int. Ed.*, **50**, 3747–3750.
- 109 Xu, L., Wang, J.X., Song, Y.L., and Jiang, L. (2008) Electrically tunable polypyrrole inverse opals with switchable stopband, conductivity, and wettability. *Chem. Mater.*, **20**, 3554–3556.
- 110 Yin, S.N., Wang, C.F., Liu, S.S., and Chen, S. (2013) Facile fabrication of tunable colloidal photonic crystal hydrogel supraballs toward a colorimetric humidity sensor. *J. Mater. Chem. C*, **1**, 4685–4690.
- 111 Diao, Y.Y., Liu, X.Y., Toh, G.W., Shi, L., and Zi, J. (2013) Multiple structural coloring of silk-fibroin photonic crystals and humidity-responsive color sensing. *Adv. Funct. Mater.*, **23**, 5373–5380.
- 112 Hu, H.B., Chen, Q.W., Cheng, K., and Tang, J. (2012) Visually readable and highly stable self-display photonic humidity sensor. *J. Mater. Chem.*, **22**, 1021–1027.
- 113 Huang, J. *et al.* (2010) Visual indication of environmental humidity by using poly(ionic liquid) photonic crystals. *Chem. Commun.*, **46**, 4103–4105.
- 114 Tian, E.T. *et al.* (2008) Colorful humidity sensitive photonic crystal hydrogel. *J. Mater. Chem.*, **18**, 1116–1122.
- 115 Kim, S.H. and Yang, S.M. (2009) Patterned polymeric domes with 3D and 2D embedded colloidal crystals using photocurable emulsion droplets. *Adv. Mater.*, **21**, 3771–3775.
- 116 Wu, L. *et al.* (2015) Printing patterned fine 3D structures by manipulating the three phase contact line. *Adv. Funct. Mater.*, **25**, 2237–2242.
- 117 Liu, F., Dong, B.Q., Liu, X.H., Zheng, Y.M., and Zi, J. (2009) Structural color change in longhorn beetles *Tmesisternus isabellae*. *Opt. Express*, **17**, 16183–16191.
- 118 Bai, L. *et al.* (2014) Bio-inspired vapor-responsive colloidal photonic crystal patterns by inkjet printing. *ACS Nano*, **8**, 11094–11100.
- 119 Arya, S.K. and Bhansali, S. (2011) Lung cancer and its early detection using biomarker-based biosensors. *Chem. Rev.*, **111**, 6783–6809.
- 120 Engel, Y. *et al.* (2010) Supersensitive detection of explosives by silicon nanowire arrays. *Angew. Chem., Int. Ed.*, **49**, 6830–6835.
- 121 Brettell, T.A., Butler, J.M., and Almirall, J.R. (2007) Forensic science. *Anal. Chem.*, **79**, 4365–4384.
- 122 Rodriguez, E., Navarro-Villoslada, F., Benito-Pena, E., Marazuela, M.D., and Moreno-Bondi, M.C. (2011) Multiresidue determination of ultratrace levels of fluoroquinolone antimicrobials in drinking and aquaculture water samples by automated online molecularly imprinted solid phase extraction and liquid chromatography. *Anal. Chem.*, **83**, 2046–2055.
- 123 Lavigne, J.J. and Anslyn, E.V. (2001) Sensing a paradigm shift in the field of molecular recognition: From selective to differential receptors. *Angew. Chem., Int. Ed.*, **40**, 3119–3130.
- 124 Minami, T. *et al.* (2012) Supramolecular sensor for cancer-associated nitrosamines. *J. Am. Chem. Soc.*, **134**, 20021–20024.
- 125 Anzenbacher, P., Li, F.Y., and Palacios, M.A. (2012) Toward wearable sensors: Fluorescent attoreactor mats as optically encoded cross-reactive sensor arrays. *Angew. Chem., Int. Ed.*, **51**, 2345–2348.

- 126 Holtz, J.H. and Asher, S.A. (1997) Polymerized colloidal crystal hydrogel films as intelligent chemical sensing materials. *Nature*, **389**, 829–832.
- 127 Ye, B.F. *et al.* (2012) Colorimetric photonic hydrogel aptasensor for the screening of heavy metal ions. *Nanoscale*, **4**, 5998–6003.
- 128 Li, M.Z. *et al.* (2008) Ultrasensitive DNA detection using photonic crystals. *Angew. Chem., Int. Ed.*, **47**, 7258–7262.
- 129 Zhao, Y.J. *et al.* (2010) Quantum-dot-tagged bioresponsive hydrogel suspension array for multiplex label-free DNA detection. *Adv. Funct. Mater.*, **20**, 976–982.
- 130 Zhao, Y.J. *et al.* (2009) Multiplex label-free detection of biomolecules with an imprinted suspension array. *Angew. Chem., Int. Ed.*, **48**, 7350–7352.
- 131 Xu, H. *et al.* (2009) Colloidal crystal beads composed of core-shell particles for multiplex bioassay. *J. Nanosci. Nanotechnol.*, **9**, 2586–2591.
- 132 Hu, J. *et al.* (2009) Photonic crystal hydrogel beads used for multiplex biomolecular detection. *J. Mater. Chem.*, **19**, 5730–5736.
- 133 Zhao, Y.J., Zhao, X.W., and Gu, Z.Z. (2010) Photonic materials for encoding and detection of biomolecules. *Proc. SPIE*, **7682**, 850964.
- 134 Asher, S.A. *et al.* (2003) Photonic crystal carbohydrate sensors: Low ionic strength sugar sensing. *J. Am. Chem. Soc.*, **125**, 3322–3329.
- 135 Xu, M., Goponenko, A.V., and Asher, S.A. (2008) Polymerized polyHEMA photonic crystals: pH and ethanol sensor materials. *J. Am. Chem. Soc.*, **130**, 3113–3119.
- 136 Li, H. *et al.* (2011) Amplifying fluorescence sensing based on inverse opal photonic crystal toward trace TNT detection. *J. Mater. Chem.*, **21**, 1730–1735.
- 137 Hou, J. *et al.* (2014) Bio-inspired photonic-crystal microchip for fluorescent ultratrace detection. *Angew. Chem., Int. Ed.*, **53**, 5791–5795.

10

Printable Semiconducting/Dielectric Materials for Printed Electronics

Sunho Jeong and Jooho Moon

10.1 Introduction

Recently, various printing technologies and printable functional materials have increasingly attracted significant interest for facilitating low-cost, large-area flexible electronics in a wide range of applications. Nozzle-based printing (including inkjet printing, aerosol-jet printing, and electrohydrodynamic-jet printing), stamp-based roll-to-roll (R2R) printing (including gravure printing, flexo-printing, gravure offset printing, and reverse offset printing), and slot-die printing have been suggested as alternative printing techniques in addition to the conventional screen printing method. At the early stage of development, research interest focused on the exploitation of highly conductive functional materials for printed electrodes. For practical realization of printed electronics, recent developments have expanded into other functional active materials for generating active/passive devices with distinctively different characteristics. The chemical/physical properties of printable functional materials substantially affect the electrical characteristics of the resulting devices that employ the printed constituent elements, as the overall performance of printed devices is determined predominantly by the properties of the component materials.

In this chapter, we review recently developed printable materials for semiconductors and dielectrics, which are the principal constituents in various electronic devices. In addition to the recent developments in materials, the relevant post-treatment processes for further improving the electrical characteristics of the resulting printed layers are discussed with the suggestion of state-of-the-art materials for printed electronics.

10.2 Printable Materials for Semiconductors

The semiconducting layer, which has an appropriate bandgap or adequate charge-carrier-generation energy levels, plays a crucial role in modulating the flow of charge carriers as a function of an applied bias in specific device architectures. As printable semiconducting materials, organic semiconductors have been recognized as prominent candidates because of their facile accessibility

toward printable fluids. Depending on the chemical properties of side functional groups positioned along a main backbone, the solubility of synthesized organic semiconductors is manifested, enabling a high solubility that is sufficient for application to various printing techniques in specific solvents. At the early stage of research, p-type organic semiconductors exhibited better mobility, with a value of approximately $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, compared with their n-type counterparts. In 2009, novel n-type organic semiconductors with a field-effect mobility of $0.1\text{--}0.65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were demonstrated even in flexo-printed, inkjet-printed, and gravure-printed transistor devices (Figure 10.1) [1]. Recently, the field-effect mobility of p-type organic semiconductors has been significantly improved (even over $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and a mobility exceeding $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported in combination with an organic dielectric with a high dielectric constant [2]. The critical impediment in the practical realization of organic semiconductors

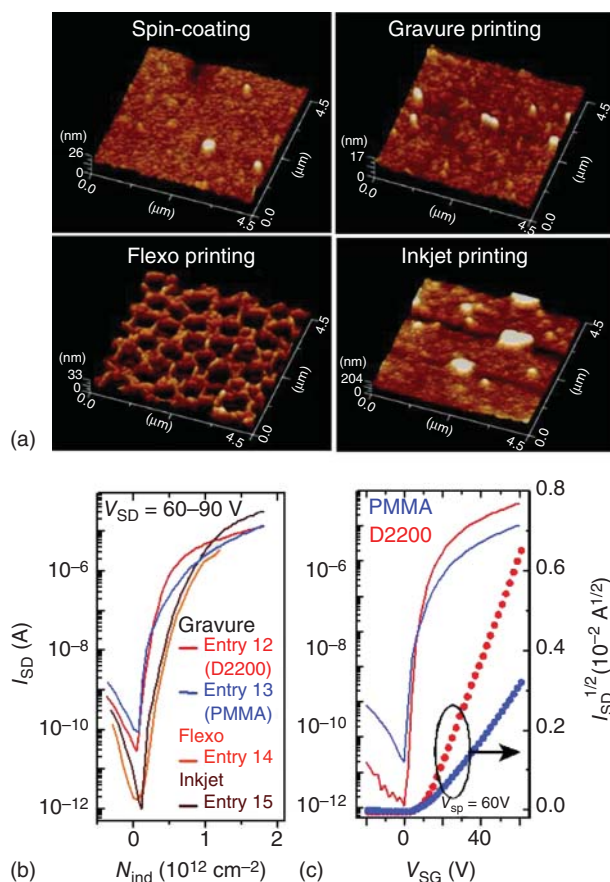


Figure 10.1 (a) Atomic force microscopy (AFM) images of spin-coated and printed films. (b) Representative TFT transfer plots of current versus carrier density (N_{ind}) of various gravure-, flexo-, and inkjet-printed devices. (c) TFT transfer plots of current versus gate voltage for representative TFTs with gravure-printed semiconductor and dielectric layers. (Yan *et al.* (2009) [1]. Reproduced with permission of Nature Publishing.)

is the stability of the electrical performance under extreme conditions. In contrast to the organic semiconductors developed earlier, the issue concerning the stability in an ambient atmosphere has been resolved by ceaseless research on high-performance organic semiconductors; however, the electrical stability remains questionable under conditions of a constant bias/current and a light illumination for a prolonged time.

For inorganic semiconductors, chalcogenide nanoparticles have gained attention, as they are capable of being dispersed in solvents depending on the chemical nature of the organic molecules adsorbed onto the surface of the nanoparticles. However, despite the intrinsic high field-effect mobilities of pure bulk chalcogenides, the mobility was limited to approximately $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [3]. As an alternative, a precursor-based chemistry was suggested, with mobilities of 16.5 and $11.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for n-type In_2Se_3 and p-type CuInTe_2 semiconductors, respectively [4, 5]. However, using this approach, a highly explosive solvent, hydrazine, was utilized for dissolving the inorganic elements without leaving behind impurities, and the resulting precursors were not stable in air, limiting their applications in practical printing processes. The air-processable chalcogenide, CdSe , was also demonstrated with mobilities of 4.0 and $41 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in combination with SiO_2 and multistacked organic–inorganic hybrid dielectrics, respectively [6]; however, the semiconducting film was formed based on a chemical bath deposition, in which the substrates were entirely immersed in a reactive solution, with no availability toward the printing process. Efforts have also been devoted toward synthesizing a precursor for deriving the silicon semiconducting film. Cyclopentasilane was reported to be usable as a silicon precursor, with the demonstration of field-effect mobilities of 108 and $6.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for spin-coated and inkjet-printed transistor devices, respectively [7]. However, the suggested precursor was also unstable in air such that practical processability under an ambient atmosphere was not possible, which is one of the critical requisites in large-area, R2R printing processes. Recently, vacuum-deposited oxide semiconductors (for instance, indium–gallium–zinc oxide) have replaced conventional silicon-based semiconductors in backplane arrays for mobile display applications. For printable, precursor-based oxide semiconductors, a high field-effect mobility was achievable with values of 7.4 and $16.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for spin-coated and inkjet-printed transistor devices, respectively [8]. However, thermal annealing at temperatures over 500°C is inevitably involved because of the thermally driven chemical reaction for forming desirable oxide semiconductors from precursors, which limits the practical accessibility even to thermally resistant glass-based substrates.

To lower the thermal-annealing temperatures, presynthesized metal-oxide nanoparticles have been used as an active channel material in thin-film transistors. The active layers were derived from a suspension containing ZnO nanoparticles, followed by drying to remove the solvents at low temperatures. However, because of the lack of interfacial electrical junctions between neighboring nanoparticles inside particulate films, the mobilities were limited to $1\text{--}2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ even with the introduction of one-dimensional rod-shaped particles and a further hydrothermal synthetic procedure [9]. The major reason why the precursor-based metal-oxide semiconductors require a large

amount of thermal energy is associated with the necessity of thermal energy for deriving the chemical conversion from hydroxide, an intermediate phase, into a corresponding metal-oxide phase as well as the thermal decomposition of impurities in the precursors. An impurity-free, Zn-hydroxide precursor produced relatively high-performance ZnO semiconductors with mobilities of 1.8 and $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after thermal annealing at 150 and 300°C , respectively [10]. To further improve the field-effect mobility, lithium was chemically doped in ZnO semiconductors derived from the Zn-hydroxide precursor, with a mobility of $7.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ after thermal annealing at 300°C (Figure 10.2) [11]. However, the hydroxide-based chemical approach is not a versatile route for synthesizing various oxide semiconductors because of the solubility limitation of hydroxide phases in solvents. In contrast, the metal-salt-based methodology could have various possibilities in selecting metal-oxide compositions including Zn–Sn–O [12], Zn–In–Sn–O [13], Sc–In–Zn–O [14], Zr–Zn–Sn–O [15], Li–Y–In–Zn–O [16], and Mg–In–Zn–O [17]. In particular, as the electrical properties of multicomponent oxide semiconductors are highly dependent on the composition of the incorporated metal cation, the controllability of the chemical composition of metal-oxide semiconductors is of paramount importance in fabricating high-performance transistor circuitries. In general, Sn, In, and Li were incorporated as mobility enhancers, and the elements such as Y, Sc, Zr, and Mg, with high bonding strengths with oxygen, were added to suppress the off-current and improve the bias stability in the resulting transistor devices.

In addition, the electrical characteristics of metal-salt-based metal-oxide semiconductors were demonstrated to be improved by the addition of appropriate catalyzers, ethylene glycol [18], and formamide [19], for successive sol–gel reactions, allowing for the enhancement of field-effect mobilities by a factor of 2.6–4.3 after thermal annealing at 400°C . By employing the double-layer-stacked Zn–In–Sn–O/In–Ga–Zn–O channel layer, a field-effect mobility of $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved after thermal annealing at 450°C (Figure 10.3) [20]. Carbon-based materials, which act as a conductive moiety, were added in metal-oxide semiconductors, allowing for mobilities of $140 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a single-walled CNT/In–Zn–O semiconductor annealed at 350°C (Figure 10.4) [21] and $23.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a graphene nanosheet/In–Ga–Zn–O semiconductor annealed at 500°C [22]. As a chemical methodology used to significantly reduce the annealing temperature, the sol–gel technique involving an exothermic combustion reaction was suggested based on the internal heat generation by vigorous coupled reactions between a fuel and an oxidizer (Figure 10.5). For a variety of oxide semiconductors (such as In–O [23], In–Zn–O [24], and Zn–Sn–O [25]), the suggested combustion-based chemistry was demonstrated to be valid with the formation of semiconducting layers with mobilities of $9.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the In_2O_3 semiconductor annealed at 325°C and of $13.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the In–Zn–O semiconductor annealed at 350°C . Apart from the effort for developing printable oxide semiconductors, various post-treatment methods have been widely exploited for activating

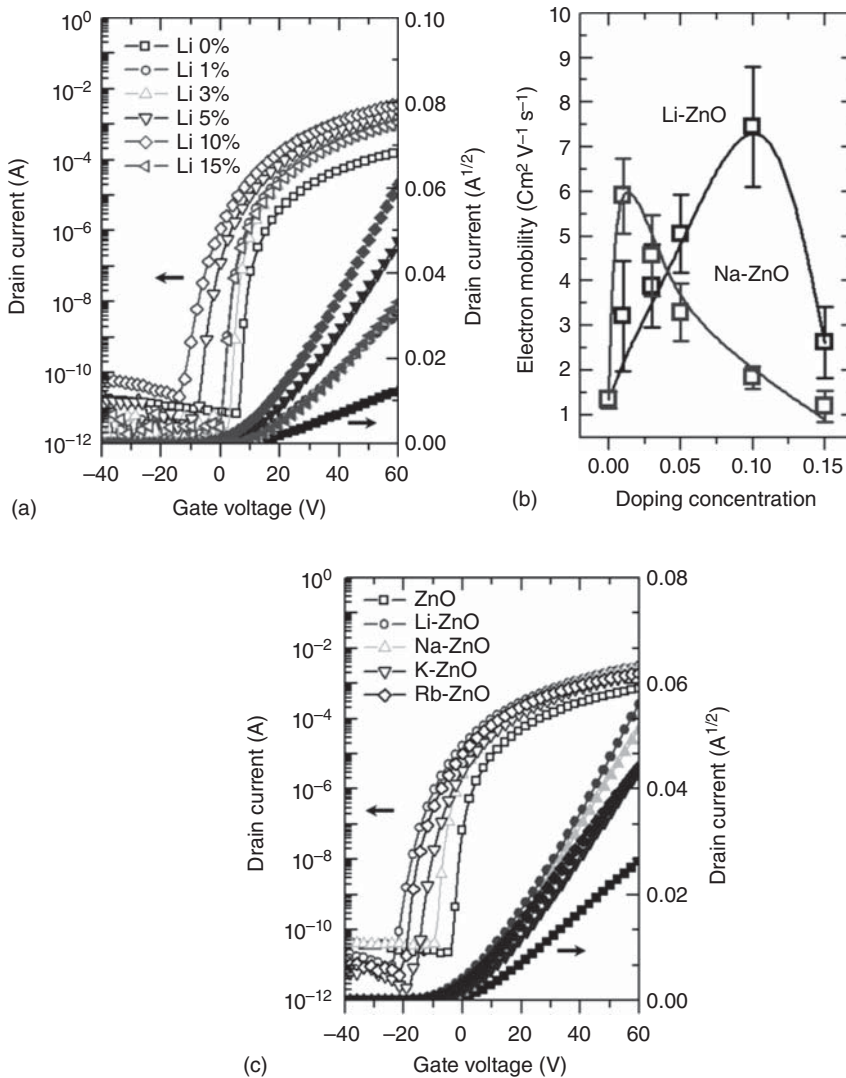


Figure 10.2 (a) Transfer characteristics of Li-doped ZnO TFTs with different doping concentrations ($V_D = 40$ V). (b) Field-effect mobility of Li and Na-doped ZnO TFTs as a function of doping concentration. (c) Transfer characteristics of the ZnO TFTs based on ZnO doped with various alkali metals (10 mol% Li, 1 mol% Na, 3 mol% K, and 1 mol% Rb). (Park *et al.* (2012) [11]. Reproduced with permission of Wiley.)

the oxide skeleton formation reaction at low temperatures by providing chemical/optical energy in combination with thermal energy. Among these methods, deep-ultraviolet irradiation facilitated the formation of device-quality In–Ga–Zn–O oxide semiconductors with mobilities of $14 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and an acceptable bias stability after thermal annealing below 150°C (Figure 10.6) [26].

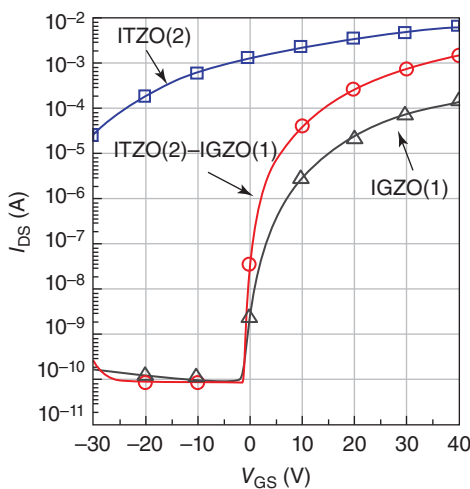


Figure 10.3 Transfer characteristics of IGZO, ITZO, and ITZO–IGZO TFTs. The number in parenthesis indicates the number of spin-coating process. (Rim *et al.* (2014) [20]. Reproduced with permission of Wiley.)

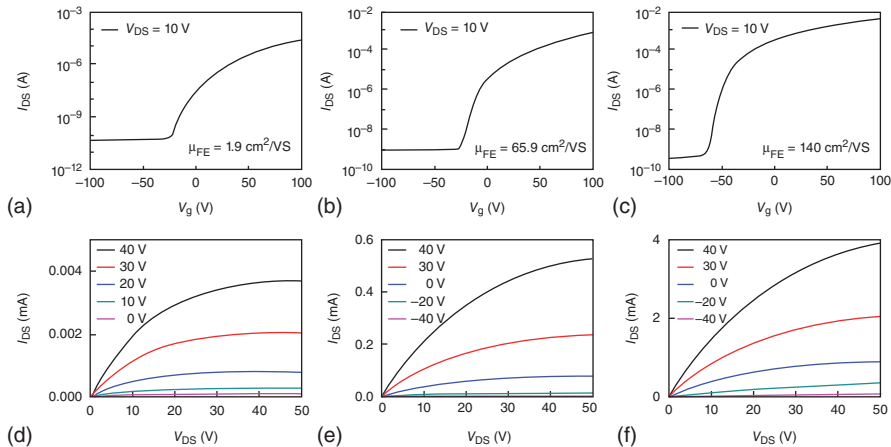


Figure 10.4 Electrical characteristics of the IZO/SWNT hybrid TFTs with different SWNT concentrations from 0 to 1 wt%. (a–c) Transfer characteristics at $V_{DS} = 10$ V: (a) 0 wt%, (b) 0.5 wt%, (c) 1 wt%. (d–f) Output characteristics: (d) 0 wt%, (e) 0.5 wt%, (f) 1 wt%. (Liu *et al.* (2012) [21]. Reproduced with permission of American Chemical Society.)

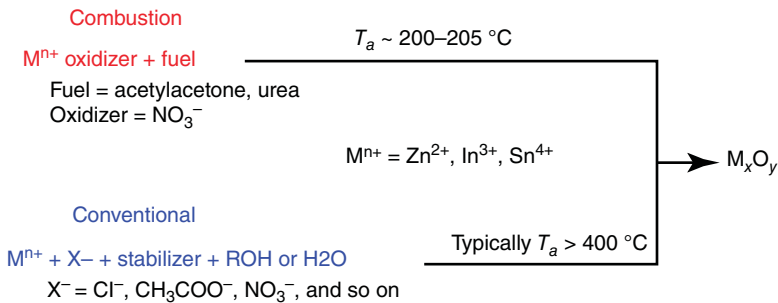


Figure 10.5 Depiction of the two different synthetic approaches: combustion chemistry-based and conventional approaches. (Kim *et al.* (2011) [23]. Reproduced with permission of Nature Publishing Group.)

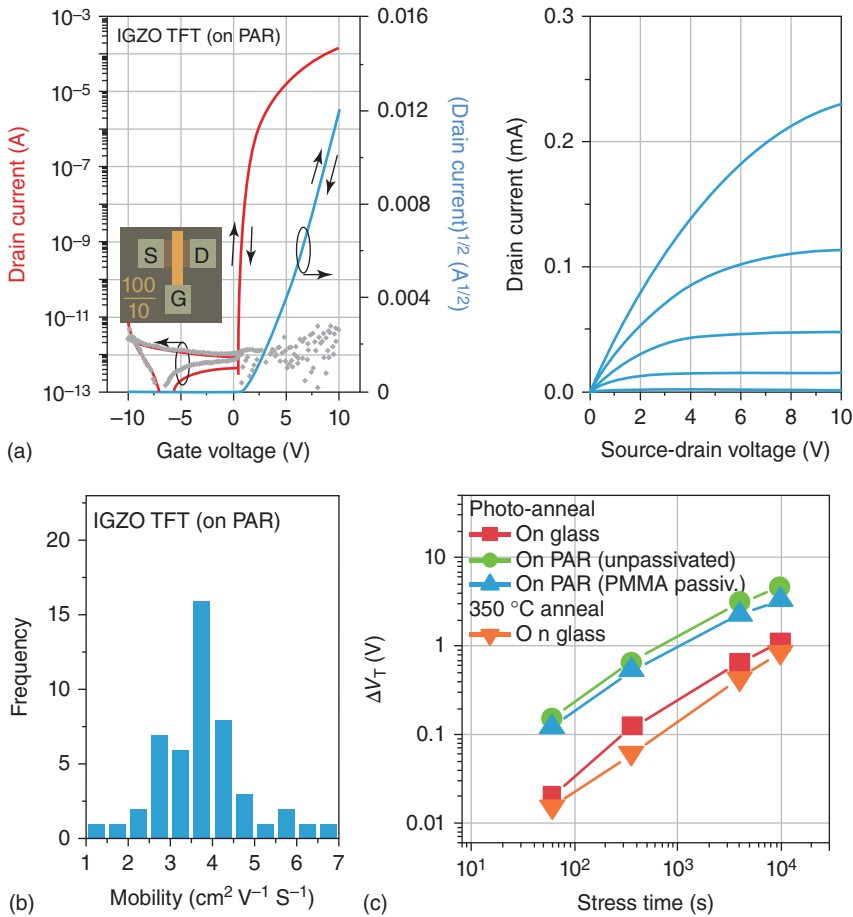


Figure 10.6 (a) Transfer and output characteristics of a photo-annealed IGZO TFT fabricated on a PAR substrate. In output curve, V_{GS} is ranging from 0 to 10 V (bottom to top), in 2-V steps. Channel length and width are 10 and 100 μm , respectively. (b) Distribution of saturation mobilities of photo-annealed IGZO TFTs on PAR (49 devices). (c) Threshold voltage shift of IGZO TFTs under positive gate-bias stress ($V_{GS} = +5 \text{ V}$, $V_{DS} = +0.1 \text{ V}$). Glass substrates are unpassivated; PAR substrates are either unpassivated (green curve) or passivated with poly(methylmethacrylate) (blue curve). (Kim *et al.* (2012) [26]. Reproduced with permission of Nature Publishing Group.)

10.3 Printable Materials for Dielectrics

In general, dielectrics can be recognized as passive materials in active device architectures, as their principal roles are to block charge-carrier transport under conditions of a highly applied bias and to separate the charge carriers on both sides of the dielectric layers. However, the degree of leakage current through a dielectric is one of the determining factors for the stable operation of the resulting devices, and the amount of separated charges determines the amount of accumulated charge carriers, which adjust the flow of charge carriers in a

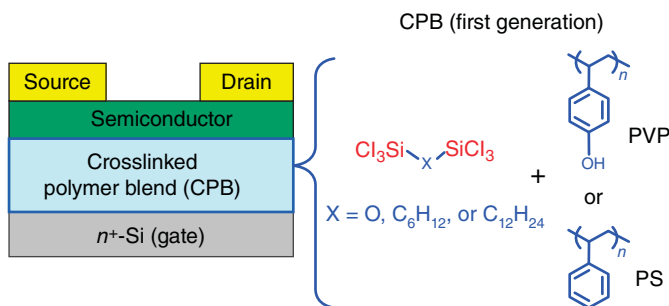


Figure 10.7 Schematic of the top-contact/bottom-gate OFET device geometry and the structures of the polymers and silane cross-linkers for the fabrication of cross-linked polymer blend gate dielectrics. (Kim *et al.* (2008) [28]. Reproduced with permission of American Chemical Society.)

semiconducting layer adjacent to a dielectric at a given operation bias condition. As a printable dielectric material, polymers soluble in specific solvents have been commonly used because of their intrinsic insulating nature even at high voltages. Representatively, polystyrene (PS) and poly(methyl methacrylate) (PMMA) dissolved in noncoordinating solvents have been widely used as printable dielectrics [27]. To date, a variety of polymeric dielectrics have been demonstrated to achieve stable operation as a gate dielectric in organic/inorganic semiconductor-based transistors. To further suppress the leakage current, a methodology for strengthening the intermolecular structural network between polymeric chains was suggested based on the incorporation of silane-based cross-linking agents for hydroxyl-containing polymer dielectrics (for instance, poly(4-vinyl)phenol) (Figure 10.7) [28].

To facilitate the devices operating at low voltages, the development of dielectrics with high capacitance is indispensable along with a low leakage current characteristic. There have been approaches based on the additional incorporation of inorganic oxide phases with a high dielectric constant and the role of a mobile charge inside dielectrics. For inorganic–organic hybrid dielectrics, the inclusion of an inorganic oxide phase tends to limit the formation of dielectrics with a high uniformity and a low leakage current. The inorganic phase is not capable of being dispersed without the formation of separated agglomerates in a polymer matrix if the surface of the inorganic phase is not functionalized properly to achieve chemical compatibility with organic materials. The chemically coupled inorganic–organic materials enabled the generation of hybrid materials with a dielectric constant reaching as high as 10.2 (a capacitance of 365 nF cm^{-2}) and a low leakage current density of $10^{-6} - 10^{-7} \text{ A cm}^{-2}$ at an electric field of 2 MV cm^{-1} by mixing a Zr precursor and a disilylalkane cross-linker under ambient conditions followed by thermal annealing at 150°C in air [29]. The multistacked, self-assembled inorganic–organic hybrid dielectrics exhibit outstanding electrical characteristics (especially in combination with inorganic metal-oxide semiconductors) [30, 31]; however, the dielectric layers were formed by a sequential, successive deposition process, which is not applicable for conventional printing processes. The ion-gel dielectrics, a type of

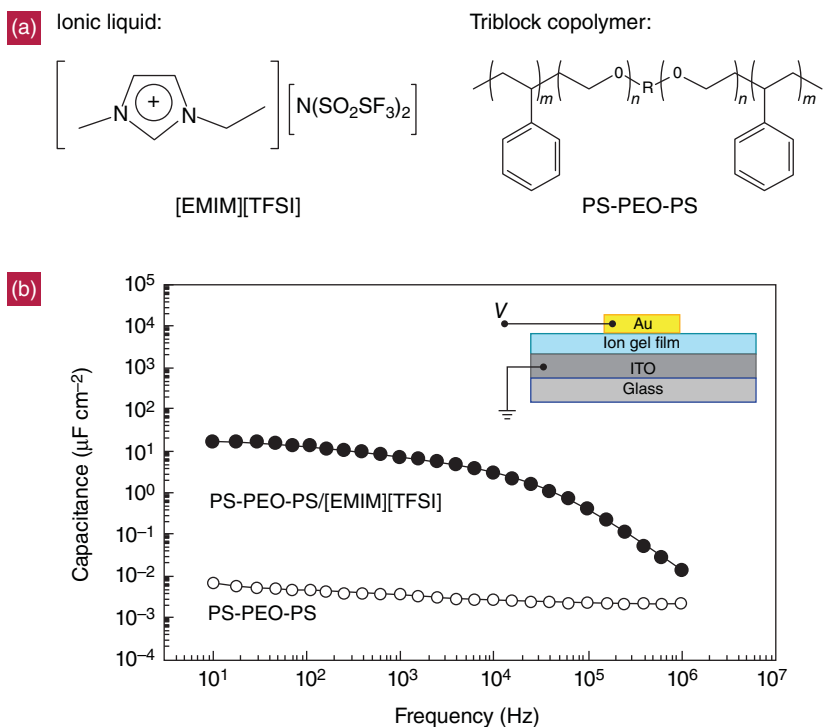


Figure 10.8 (a) Ionic liquid and triblock copolymer: [EMIM][TFSI] and PS-PEO-PS, respectively. (b) Frequency dependence of the specific capacitance of triblock copolymer and ion-gel film. (Cho *et al.* (2008) [32]. Reproduced with permission of Nature Publishing Group.)

polymer electrolyte, allow for large capacitances associated with the formation of an electrical double layer at the electrode–electrolyte interfaces (Figure 10.8) [32, 33]. A high capacitance of $\sim 20 \mu\text{F cm}^{-2}$ was achieved under a low-frequency condition, and even with the dependency of the capacitance on the frequency, a relatively high capacitance of $1 \mu\text{F cm}^{-2}$ was maintained at a frequency of 10 kHz. Because of this high capacitance characteristic, transistors employing ion-gel dielectrics have been demonstrated to be operated at gate voltages as low as 3 V, even if they are deposited selectively using printing techniques (Figure 10.9).

In addition to organic dielectrics, inorganic dielectrics have been exploited with the critical advantage of a high dielectric constant. Similar to metal-salt-based oxide semiconductors, sol-gel chemistries have been applied to oxide dielectrics. For metal oxides as a dielectric, there is a critical trade-off behavior between the dielectric constant and leakage current. Metal oxides with a high dielectric constant tend to be electrically leaky with a high gate current in transistor architectures. The representative metal oxides, with intermediate properties in terms of dielectric constant and leakage current, are Al_2O_3 - and ZrO_2 -based ones [34–36]. Zr-doped AlO_x dielectrics were demonstrated to exhibit a dielectric constant of 11.8 (a capacitance of 110 nF cm^{-2} at a frequency of 1 MHz) and a low leakage current density of $10^{-6} \text{ A cm}^{-2}$ at an electric field of 2 MV cm^{-1}

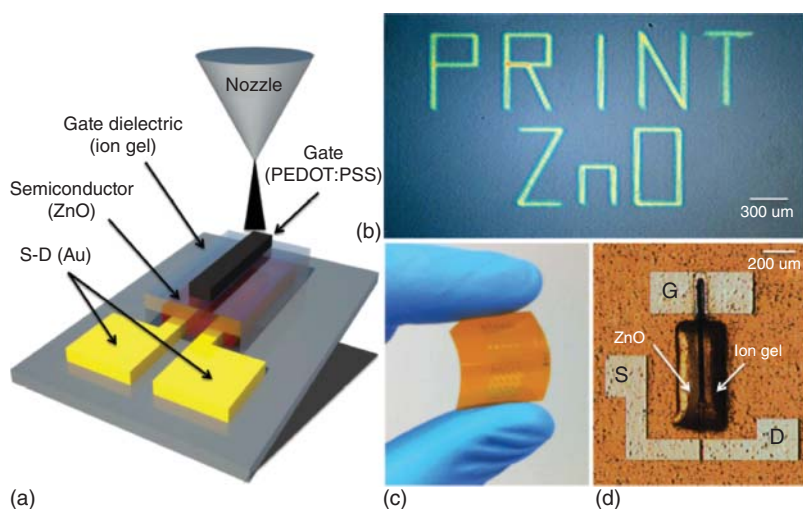


Figure 10.9 (a) Scheme of printed ZnO TFTs with ion-gel gate insulator (45-nm-thick photolithographically patterned Au source-drain electrodes with $W/L = 500/25 \mu\text{m}$ and printed 500-nm-thick PEDOT:PSS gate electrode). Diagram is not to scale. (b) Optical micrograph of an aerosol-jet-printed ZnO pattern. The minimum width of the printed lines is about $50 \mu\text{m}$. (c) Optical image of a flexible ZnO device on kapton substrate. (d) A magnified image of a single device, where all the functional layers can be distinguished. (Hong *et al.* (2013) [33]. Reproduced with permission of Wiley.)

(Figure 10.10) [34]. However, one of the critical impediments for printable metal-oxide dielectrics is the necessity of thermal annealing at temperatures as high as 400°C . This necessity is caused by the chemical conversion of the metal-salt precursors into corresponding metal-oxide frameworks, which is identical to the case of metal-salt-based oxide semiconductors. Combustion chemistry, by which internal heat as another energy source is generated by a combinatorial reaction between incorporated reactants, has been also applied to oxide gate dielectrics. By coupling aluminum nitrate (as a oxidizer) and acetylacetonate (as a fuel) in an alcoholic solution, a 45-nm-thick Al_2O_3 dielectric with a capacitance of 377 nF cm^{-2} was obtained by thermal annealing at 300°C [37]. The incorporation of self-combustive precursors, aluminum nitrate (as a oxidizer) and aluminum acetylacetonate (as a fuel), enabled a more efficient combustive reaction, and the composite dielectrics derived by thermal annealing at 250°C exhibited a dielectric constant of 8.7 and leakage current of $\sim 10^{-9} \text{ A cm}^{-2}$ at 2 MV cm^{-1} through hybridization with an organoalkoxide, 3-glycidoxylpropyltrimethoxysilane [38]. To further improve the electrical characteristics of oxide-based gate dielectrics with low-temperature processability, novel chemical/physical strategies need to be exploited to modify the chemical synthetic path for metal-oxide dielectrics and provide another energy source to trigger the chemical conversion reactions.

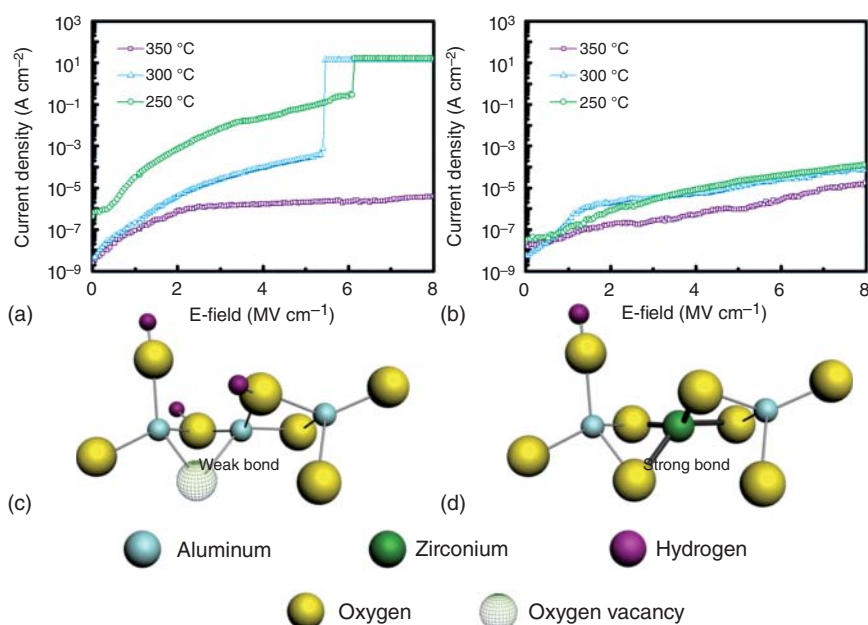


Figure 10.10 Effect of zirconium doping on the electrical properties of the solution-processed amorphous alumina thin film. Leakage current density versus electric field plots for (a) AlO_x and (b) zirconium-doped aluminum oxide (ZAO). Schematics showing the conceptual structural features of (c) AlO_x and (d) ZAO. AlO_x contains weakly bonded oxygen-associated lattice defects or hydroxide due to their weak bonding to oxygen, which are replaced with strongly bonded oxygen upon the addition of a Zr cation. (Yang *et al.* (2013) [34]. Reproduced with permission of Royal Society of Chemistry.)

10.4 Conclusions

In the recent decade, a variety of printable semiconducting/dielectric materials have been developed with significant improvement in terms of the properties of the materials themselves and the electrical characteristics of the resulting printed functional layers along with sophisticated consideration of their cost-effectiveness and large-area processability. To date, a variety of organic, inorganic, hybrid, and carbon materials have been suggested to satisfy the various chemical/physical requisites of printed electronics. With the use of newly developed post-treatment techniques, the electrical performances of printed materials have been substantially enhanced, approaching the technical levels necessary for practical applications. With the recent progress in printable materials, the significant advantages of printed circuitries, which have not been obtainable in applications based on vacuum-deposition processes and photolithography-involved patterning processes, have emerged in low-cost, large-area, flexible electronics. With the development of chemical/physical

approaches used to adjust the required material properties on demand, the industrial fields of printed electronics would be extensively widened with a promising forecast. It is highly expected that the further development of novel semiconducting/dielectric functional materials in combination with well-designed printing techniques will open up heretofore unrecognized possibilities in new fields of printed electronics.

References

- 1 Yan, H., Chen, Z., Zheng, Y., Newman, C., Quinn, J.R., Dötz, F., Kastler, M., and Facchetti, A. (2009) A high-mobility electron-transporting polymer for printed transistors. *Nature*, **457** (7230), 679–686.
- 2 Kim, G., Kang, S.-J., Dutta, G.K., Han, Y.-K., Shin, T.J., Noh, Y.-Y., and Yang, C. (2014) A thienoisindigo-naphthalene polymer with ultrahigh mobility of $14.4 \text{ cm}^2/\text{V}\cdot\text{s}$ that substantially exceeds benchmark values for amorphous silicon semiconductors. *J. Am. Chem. Soc.*, **136** (26), 9477–9483.
- 3 Ridley, B.A., Nivi, B., and Jacobson, J.M. (1999) All-inorganic field effect transistors fabricated by printing. *Science*, **286** (5440), 746–749.
- 4 Mitzi, D.B., Copel, M., and Chey, S.J. (2005) Low-voltage transistor employing a high-mobility spin-coated chalcogenide semiconductor. *Adv. Mater.*, **17** (10), 1285–1289.
- 5 Mitzi, D.B., Copel, M., and Murray, C.E. (2006) High-mobility p-type transistor based on a spin-coated metal telluride semiconductor. *Adv. Mater.*, **18** (18), 2448–2452.
- 6 Byrne, P.D., Facchetti, A., and Marks, T.J. (2008) High-performance thin-film transistors from solution-processed cadmium selenide and a self-assembled multilayer gate dielectric. *Adv. Mater.*, **20** (12), 2319–2324.
- 7 Shimoda, T., Matsuki, Y., Furusawa, M., Aoki, T., Yudasaka, I., Tanaka, H., Iwasawa, H., Wang, D., Miyasaka, M., and Takeuchi, Y. (2006) Solution-processed silicon films and transistors. *Nature*, **440** (7085), 783–786.
- 8 Lee, D.-H., Chang, Y.-J., Herman, G.S., and Chang, C.-H. (2007) A general route to printable high-mobility transparent amorphous oxide semiconductors. *Adv. Mater.*, **19** (6), 843–847.
- 9 Sun, B., Peterson, R.L., Sirringhaus, H., and Mori, K. (2007) Low-temperature sintering of in-plane self-assembled ZnO nanorods for solution-processed high-performance thin film transistors. *J. Phys. Chem. C*, **111** (51), 18831–18835.
- 10 Meyers, S.T., Anderson, J.T., Hung, C.M., Thompson, J., Wager, J.F., and Keszler, D.A. (2008) Aqueous inorganic inks for low-temperature fabrication of ZnO TFTs. *J. Am. Chem. Soc.*, **130** (51), 17603–17609.
- 11 Park, S.Y., Kim, B.J., Kim, K., Kang, M.S., Lim, K.-H., Lee, T.I., Myoung, J.M., Baik, H.K., Cho, J.H., and Kim, Y.S. (2012) Low-temperature,

- solution-processed and alkali metal doped ZnO for high-performance thin-film transistors. *Adv. Mater.*, **24** (6), 834–838.
- 12 Jeong, S., Jeong, Y., and Moon, J. (2008) Solution-processed zinc-tin oxide semiconductor for thin-film transistors. *J. Phys. Chem. C*, **112** (30), 11082–11085.
 - 13 Kim, M.-G., Kim, H.S., Ha, Y.-G., He, J., Kanatzidis, M.G., Facchetti, A., and Marks, T.J. (2010) High-performance solution-processed amorphous zinc–indium–tin oxide thin-film transistors. *J. Am. Chem. Soc.*, **132** (30), 10352–10364.
 - 14 Choi, Y., Kim, G.H., Jeong, W.H., Bae, J.H., Kim, H.J., Hong, J.-M., and Yu, J.-W. (2010) Carrier-suppressing effect of scandium in InZnO systems for solution-processed thin film transistors. *Appl. Phys. Lett.*, **97** (16), 162102.
 - 15 Rim, Y.S., Kim, D.L., Jeong, W.H., and Kim, H.J. (2010) Effect of Zr addition on ZnSnO thin-film transistors using a solution process. *Appl. Phys. Lett.*, **97** (23), 233502.
 - 16 Koo, C.Y., Song, K., Jung, Y., Yang, W., Kim, S.-H., Jeong, S., and Moon, J. (2012) Enhanced performance of solution-processed amorphous LiYInZnO thin-film transistors. *ACS Appl. Mater. Interfaces*, **4** (3), 1456–1461.
 - 17 Kim, G.H., Jeong, W.H., Ahn, B.D., Shin, H.S., Kim, H.J., Kim, H.J., Ryu, M.-K., Park, K.-B., Seon, J.-B., and Lee, S.-Y. (2010) Investigation of the effects of Mg incorporation into InZnO for high-performance and high-stability solution-processed thin film transistors. *Appl. Phys. Lett.*, **96** (16), 163506.
 - 18 Jeong, S., Lee, J.-Y., Lee, S.S., Oh, S.-W., Lee, H.H., Seo, Y.-H., Ryu, B.-H., and Choi, Y. (2011) Chemically improved high performance printed indium gallium zinc oxide thin-film transistors. *J. Mater. Chem.*, **21** (43), 17066–17070.
 - 19 Jeong, S., Lee, J.-Y., Lee, S.S., Seo, Y.-H., Kim, S.-Y., Park, J.-U., Ryu, B.-H., Yang, W., Moon, J., and Choi, Y. (2013) Metal salt-derived In–Ga–Zn–O semiconductors incorporating formamide as a novel co-solvent for producing solution-processed, electrohydrodynamic-jet printed, high performance oxide transistors. *J. Mater. Chem. C*, **1** (27), 4236–4243.
 - 20 Rim, Y.S., Chen, H., Kou, X., Duan, H.-S., Zhou, H., Cai, M., Kim, H.J., and Yang, Y. (2014) Boost Up mobility of solution-processed metal oxide thin-film transistors via confining structure on electron pathways. *Adv. Mater.*, **26** (25), 4273–4278.
 - 21 Liu, X., Wang, C., Cai, B., Xiao, X., Guo, S., Fan, Z., Li, J., Duan, X., and Liao, L. (2012) Rational design of amorphous indium zinc oxide/carbon nanotube hybrid film for unique performance transistors. *Nano Lett.*, **12** (7), 3596–3601.
 - 22 Dai, M.-K., Lian, J.-T., Lin, T.-Y., and Chen, Y.-F. (2013) High-performance transparent and flexible inorganic thin film transistors: a facile integration of graphene nanosheets and amorphous InGaZnO. *J. Mater. Chem. C*, **1** (33), 5064–5071.
 - 23 Kim, M.-G., Kanatzidis, M.G., Facchetti, A., and Marks, T.J. (2011) Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing. *Nat. Mater.*, **10** (5), 382–388.

- 24 Kang, Y.H., Jeong, S., Ko, J.M., Lee, J.-Y., Choi, Y., Lee, C., and Cho, S.Y. (2014) Two-component solution processing of oxide semiconductors for thin-film transistors via self-combustion reaction. *J. Mater. Chem. C*, **2** (21), 4247–4256.
- 25 Kim, S.J., Song, A.R., Lee, S.S., Nahm, S., Choi, Y., Chung, K.-B., and Jeong, S. (2015) Independent chemical/physical role of combustive exothermic heat in solution-processed metal oxide semiconductors for thin-film transistors. *J. Mater. Chem. C*, **3** (7), 1457–1462.
- 26 Kim, Y.-H., Heo, J.-S., Kim, T.-H., Park, S., Yoon, M.-H., Kim, J., Oh, M.S., Yi, G.-R., Noh, Y.-Y., and Park, S.K. (2012) Flexible metal-oxide devices made by room-temperature photochemical activation of sol–gel films. *Nature*, **489** (7414), 128–132.
- 27 Kim, C., Facchetti, A., and Marks, T.J. (2007) Polymer gate dielectric surface viscoelasticity modulates pentacene transistor performance. *Science*, **318** (5847), 76–80.
- 28 Kim, C., Wang, Z., Choi, H.-J., Ha, Y.-G., Facchetti, A., and Marks, T.J. (2008) Printable cross-linked polymer blend dielectrics. Design strategies, synthesis, microstructures, and electrical properties, with organic field-effect transistors as testbeds. *J. Am. Chem. Soc.*, **130** (21), 6867–6878.
- 29 Ha, Y.-G., Jeong, S., Wu, J., Kim, M.-G., Dravid, V.P., Facchetti, A., and Marks, T.J. (2010) Flexible low-voltage organic thin-film transistors enabled by low-temperature, ambient solution-processable inorganic/organic hybrid gate dielectrics. *J. Am. Chem. Soc.*, **132** (49), 17426–17434.
- 30 Liu, J., Buchholz, D.B., Chang, R.P.H., Facchetti, A., and Marks, T.J. (2010) High-performance flexible transparent thin-film transistors using a hybrid gate dielectric and an amorphous zinc indium Tin oxide channel. *Adv. Mater.*, **22** (21), 2333–2337.
- 31 Ha, Y.-G., Everaerts, K., Hersam, M.C., and Marks, T.J. (2014) Hybrid gate dielectric materials for unconventional electronic circuitry. *Acc. Chem. Res.*, **47** (4), 1019–1028.
- 32 Cho, J.H., Lee, J., Xia, Y., Kim, B.S., He, Y., Renn, M.J., Lodge, T.P., and Frisbie, C.D. (2008) Printable ion-gel gate dielectrics for low-voltage polymer thin-film transistors on plastic. *Nat. Mater.*, **7** (11), 900–906.
- 33 Hong, K., Kim, S.H., Lee, K.H., and Frisbie, C.D. (2013) Printed, sub-2 V ZnO electrolyte gated transistors and inverters on plastic. *Adv. Mater.*, **25** (25), 3413–3418.
- 34 Yang, W., Song, K., Jung, Y., Jeong, S., and Moon, J. (2013) Solution-deposited Zr-doped AlOx gate dielectrics enabling high-performance flexible transparent thin film transistors. *J. Mater. Chem. C*, **1** (27), 4275–4282.
- 35 Afouxenidis, D., Mazzocco, R., Vourlias, G., Livesley, P.J., Krier, A., Milne, W.I., Kolosov, O., and Adamopoulos, G. (2015) ZnO-based thin film transistors employing aluminum titanate gate dielectrics deposited by spray pyrolysis at ambient air. *ACS Appl. Mater. Interfaces*, **7** (13), 7334–7341.

- 36 Lee, W.-J., Park, W.-T., Park, S., Sung, S., Noh, Y.-Y., and Yoon, M.-H. (2015) Large-scale precise printing of ultrathin Sol–Gel oxide dielectrics for directly patterned solution-processed metal oxide transistor arrays. *Adv. Mater.*, **27** (34), 5043–5048.
- 37 Wang, H., Sun, T., Xu, W., Xie, F., Ye, L., Xiao, Y., Wang, Y., Chen, J., and Xu, J. (2014) Low-temperature facile solution-processed gate dielectric for combustion derived oxide thin film transistors. *RSC Adv.*, **4**, 54729–54739.
- 38 Bae, E.J., Kang, Y.H., Han, M., Lee, C., and Cho, S.Y. (2014) Soluble oxide gate dielectrics prepared using the self-combustion reaction for high-performance thin-film transistors. *J. Mater. Chem. C*, **2**, 5695–5703.

11

Low Melting Point Metal or Its Nanocomponents as Functional 3D Printing Inks

Lei Wang and Jing Liu

11.1 Introduction of Metal 3D Printing

As two representative cases of additive manufacturing technology, printed electronics and 3D printing are rapidly reshaping the world in a wide variety of areas including electronic manufacturing [1], chemical synthesis [2], tissue engineering [3, 4], microfluidics [5], and so on. Conventional metal 3D printing is mainly based on high melting point metal (such as Ti, Ti-6Al-4 V, etc.) powders with expensive manufacturing cost. And laser sintering (LS), laser melting (LM), and laser metal deposition (LMD) are among three most prevailing printing techniques [6]. The printing quality is affected by a series of factors including the chemical constituent of the ink, particle size, powder flowability, laser power, scan speed, and so on [7, 8]. Low melting point metal-based additive technology, which has unfortunately been neglected by the researchers for a very long time, is arousing great research interest recently both in academy and industry. Several representative techniques have been gradually developed. Zheng *et al.* [9, 10] proposed a direct writing strategy to make liquid metal circuits, which has important significance in the current electronic manufacturing industry. Zhang *et al.* [11] presented an atomized spray printing method to quickly fabricate liquid metal patterns on nearly all solid surfaces. Jin *et al.* [12] demonstrated an injectable printing method for directly making 3D medical electronics inside the biological body through injecting liquid metal and biocompatible packaging material together. Kramer *et al.* [13] introduced a masked deposition method for producing hyperelastic electronic circuits composed of elastomer film embedded with microchannels of Ga-In alloy. Fassler and Majidi [14] developed a method to fabricate liquid metal electronics with freeze casting. Figure 11.1 presents four Ga-In liquid alloy patterns fabricated with atomized spray printing, direct writing, masked deposition, and injection casting methods, respectively.

All the above-mentioned studies stimulated various kinds of innovative 3D printing methods with liquid metal as the ink. In this chapter, the typical properties of liquid metal and several theoretical models for characterizing nanometal fluids was summarized. To exhibit latest research progress made in 3D metal printing, a liquid-phase printing method as initiated in current laboratory was particularly discussed with a kind of low melting point metal, $\text{Bi}_{35}\text{In}_{48.6}\text{Sn}_{16}\text{Zn}_{0.4}$, as the functional ink.

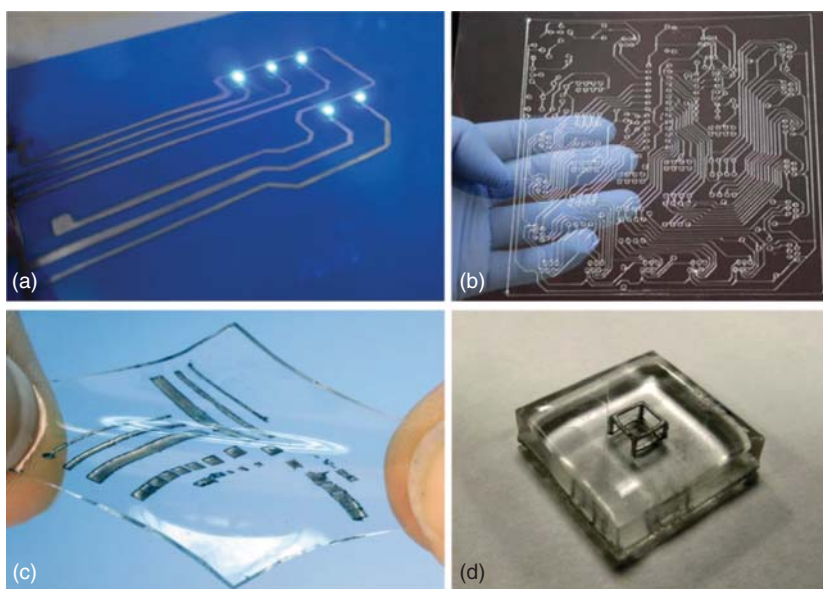


Figure 11.1 (a) A printed LED circuit on a plastic film through atomized spray printing method. (Zhang *et al.* (2014) [11]. Reproduced with permission. Copyright 2014, Springer); (b) a printed circuit on PVC substrate via direct writing method. (Zheng *et al.* (2014) [10]. Reproduced with permission. Copyright 2014, Nature Publishing Group); (c) a liquid-embedded-elastomer patterned with Ga–In liquid metal. (Kramer *et al.* (2013) [13]. Reproduced with permission. Copyright 2013, Wiley-VCH); (D) a liquid metal cube antenna fabricated with injection casting method. (Fassler and Majidi (2013) [14]. Reproduced with permission. Copyright 2013, RSC Publishing.)

11.2 Low Melting Point Metal Ink

11.2.1 Liquid Metal Printing Ink

Low melting point (typically less than 100 °C) metal, especially room temperature liquid metal, is a kind of newly emerging functional material that has attracted broad attention and research interests in recent years. Table 11.1 lists several typical physical properties of two liquid metal inks (Ga and $\text{Ga}_{62.5}\text{In}_{21.5}\text{Sn}_{16}$) and two conventional fluids (water and ethylene), respectively. It can be seen that the liquid metal has one order of surface tension larger and one order of specific capacity lower than that of conventional fluids. Figure 11.2 shows the liquid metal nanoparticles generated by the ultrasonic disruption method, from which it can be seen that the nanoparticles exhibit sphere-like shape due to its large surface tension. Besides, the liquid metal has superior thermal and electrical properties compared to many conventional fluids. These properties make it an excellent printing ink in additive manufacturing.

Figure 11.3 presents a schematic for the injectable 3D printing of medical electronics [14]. The used liquid metal and the packaging inks are $\text{Ga}_{67}\text{In}_{20.5}\text{Sn}_{12.5}$ and gelatin, respectively. A syringe needle was adopted to shape the electrode

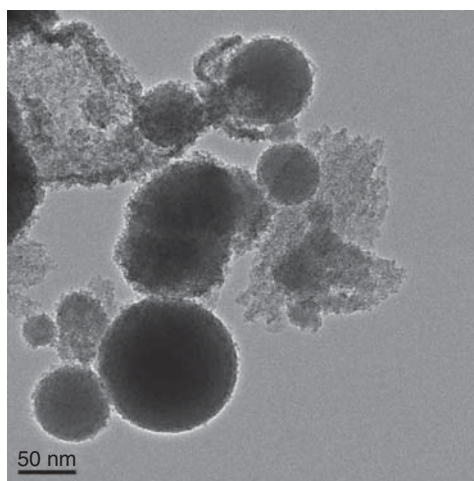
Table 11.1 Physical properties of conventional fluids and liquid metal [15–20].

Property	Conventional fluid		Liquid metal fluid	
	Water	Ethylene glycol	Ga	Ga _{62.5} In _{21.5} Sn ₁₆
Density (kg m ⁻³)	998	1132	6048 ^{a)}	6440
Surface tension (mN m ⁻¹)	72.8	48.4	707 ^{b)}	718
Viscosity (10 ⁻⁶ m ² s ⁻¹)	1.0	0.19	0.23	0.37
Melting point (°C)	0	-12.6	29.8	11
Specific heat capacity (J kg ⁻¹ °C ⁻¹)	4182	2349	370 ^{b)}	
Thermal conductivity (W m ⁻¹ °C ⁻¹)	0.6	0.258	29.4 ^{b)}	16.5
Electrical conductivity (10 ⁷ S m ⁻¹)	5.5 × 10 ^{-13c)}		0.22	0.38

a) At 77 °C.

b) At 50 °C.

c) Ultrapure water.

Figure 11.2 TEM image of the liquid metal nanoparticles.

mold, followed by injecting the liquid metal ink. A fabricated electrode within the porcine tissue is shown in Figure 11.3b.

Figure 11.4 presents the injectable 3D printing of low melting point metal to quickly form bone cement at the target site. Here, Bi₃₅In_{48.6}Sn₁₆Zn_{0.4} was adopted as the metal ink. The metal bone cement is made through directly injecting liquid metal (Bi₃₅In_{48.6}Sn₁₆Zn_{0.4} in molten state) and allied packaging material in the porcine tissue [21]. As the liquid metal is cooled down, it would become solidified and the metal bone cement can be formed, which then will play a supporting role.

Figure 11.5 exhibits the comparisons of the thermal conductivity and electrical conductivity between liquid metal and other materials. It can be seen that the thermal conductivities of Ga, Ga_{62.5}In_{21.5}Sn₁₆ and Bi₃₅In_{48.6}Sn₁₆Zn_{0.4} are two orders larger than that of water, while one order lower than that of Cu and Ag. And the electrical conductivities of the three low melting metals are one order

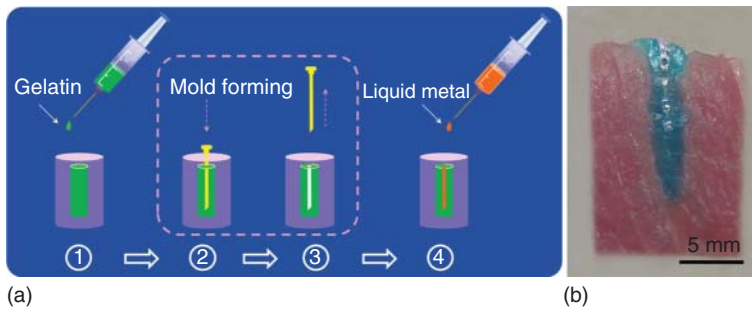


Figure 11.3 Injectable 3D printing of medical electronics. (a) The fabrication process of implantable bio-electrode. Here, (1) denotes the formed packaging domain; (2) and (3) represent the fabrication process of electrode mode; (4) denotes the formed electrode within the packaging domain by injecting liquid metal ink; (b) a printed implantable electrode within the in vitro porcine tissues. (Jin *et al.* (2013) [12]. Reproduced with permission of Nature Publishing Group.)

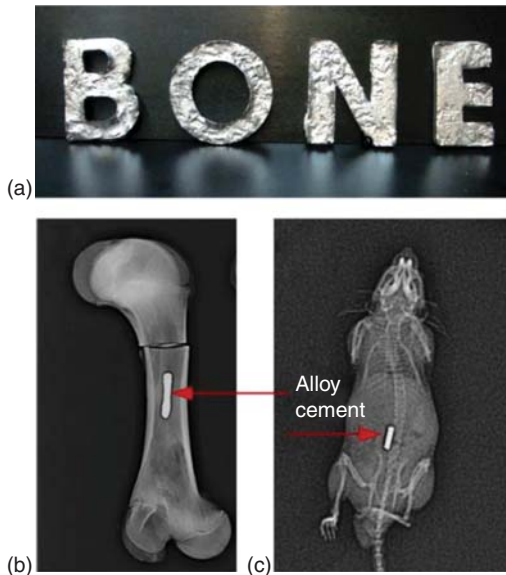


Figure 11.4 Injectable 3D printing of metal bone cement. (a) A demonstrated molding of alloy cement in the shape of "BONE"; (b) X-ray imaging of the bone cavity filled with alloy cement; (c) X-ray imaging of the mouse with the alloy cement implanted subcutaneously [21]. (Yi *et al.* (2014) [21]. Reproduced with permission of Elsevier.)

lower than that of Cu and Ag. As the thermal and electrical properties of low melting point metals are typically much smaller than that of metals with excellent properties, nanoliquid metal mixed with liquid metal and highly conductive nanoparticles serves as a good candidate ink for printed electronics or 3D printing of metal structures.

11.2.2 Nanoliquid Metal

Several theoretical models have been established to evaluate the physical properties especially thermal properties of nanofluids through calculating the effective thermal conductivity, such as Maxwell-Garnett model [22], Lu–Lin model [23],

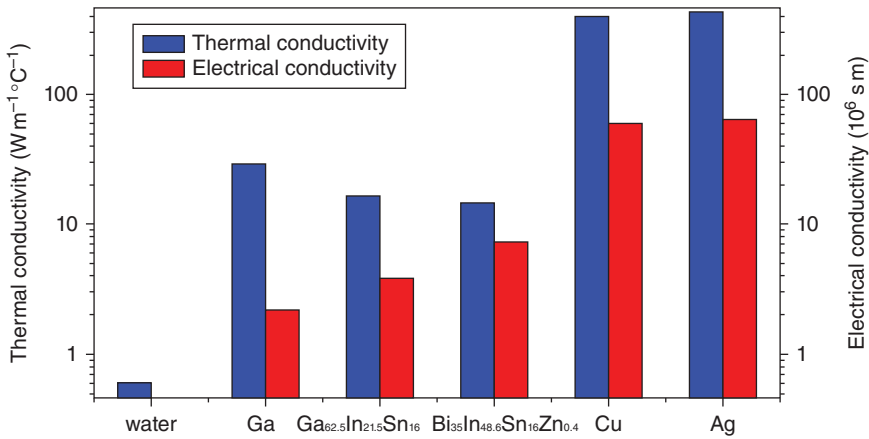


Figure 11.5 Comparisons of the thermal conductivity and electrical conductivity between liquid metal and other materials.

Table 11.2 Typical models for calculating effective thermal conductivity of nanofluids.

Models	Expressions	Remarks
Maxwell [22]	$\frac{\kappa_{\text{eff}}}{\kappa_f} = 1 + \frac{3(\alpha-1)\nu}{(\alpha+2) - (\alpha+1)\nu}$	Spherical particles are considered
Lu–Lin [23]	$\frac{\kappa_{\text{eff}}}{\kappa_f} = 1 + a\nu + b\nu^2$	Spherical and nonspherical particles are considered
Bruggeman [24]	$\frac{\kappa_{\text{eff}}}{\kappa_f} = \frac{1}{4} \{ (3\nu - 1)k_1 + (2 - 3\nu) + \sqrt{\Delta} \}$ $\Delta = (3\nu - 1)k_1^2 + (2 - 3\nu)^2 + 2[2 + 9\nu(1 - \nu)]k_1$	The clustering of nanoparticles and the surface adsorption are considered

κ_{eff} is the effective thermal conductivity of solid/liquid suspensions; κ_f is the thermal conductivity of base fluid; κ_p is the thermal conductivity of nanoparticle; $\alpha = \kappa_p / \kappa_f$ is the thermal conductivity ratio; ν is the particle volume fraction.

Bruggeman model [24], to name just a few. The calculation formula and applicable conditions of these three models are listed in Table 11.2. Figure 11.6 shows the effective thermal conductivity calculation result of nanoliquid metal mixed with liquid gallium and nanoparticles by using the Bruggeman model. The thermal conductivities of the added carbon nanotube, gold, silver, and copper are $3000 \text{ W m}^{-1} \text{ K}^{-1}$, $315 \text{ W m}^{-1} \text{ K}^{-1}$, $427 \text{ W m}^{-1} \text{ K}^{-1}$, and $386 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The effective thermal conductivity enhancement ratio of the nanoliquid metal is more than 1.6 when the volume fraction of the added nanoparticles reaches 20% [25]. Other physical properties such as electrical behaviors can also be interpreted by the same way as that of thermal properties, which will not be presented here.

Up to now, there are few attempts in preparing low melting point metal-based nanocomposites, which may be due to the fusible properties of the low

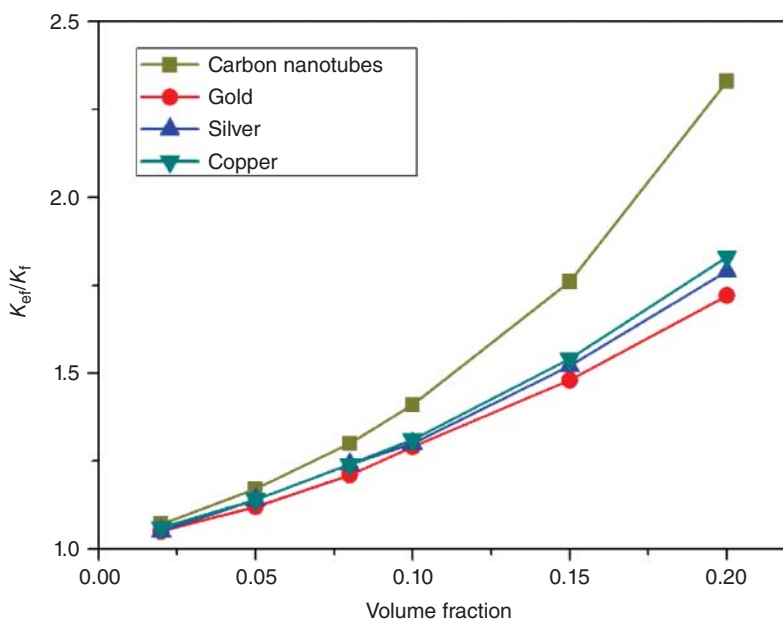


Figure 11.6 The relation between the thermal conductivity enhancement ratio and the volume fraction of different nanoparticles in liquid-gallium suspensions. (Ma and Liu (2007) [25]. Reproduced with permission of Elsevier.)

melting point alloys. In this respect, fabrication methods of high-temperature metal-based nanocomposites such as severe plastic deformation [26], stir casting [27], ball milling [28] and microwave sintering powder metallurgy [29] can be referred to make low melting point metal-based nanocomposites.

11.3 Liquid-Phase 3D Printing

Conventional 3D metal printing is generally a time-consuming process, for the cooling environment is usually in air or vacuum. Such printing processes can be called dry printing method. To significantly improve the cooling efficiency of the printed metallic part and thus the fabrication speed, a liquid-phase 3D printing method for quickly fabricating metal objects was proposed by current lab at Technical Institute of Physics and Chemistry, Chinese Academy of Sciences [30]. In that method, the metal deposition and formation process is carried out in liquid-phase cooling fluid, which can be water, ethanol, acid, and alkaline electrolyte, and so on.

11.3.1 Fabrication Scheme

The experimental device for liquid-phase printing is illustrated in Figure 11.7. The printing method of pneumatic type fused deposition modeling was adopted. A low melting point alloy $\text{Bi}_{35}\text{In}_{48.6}\text{Sn}_{16}\text{Zn}_{0.4}$ is chosen as the printing ink and its

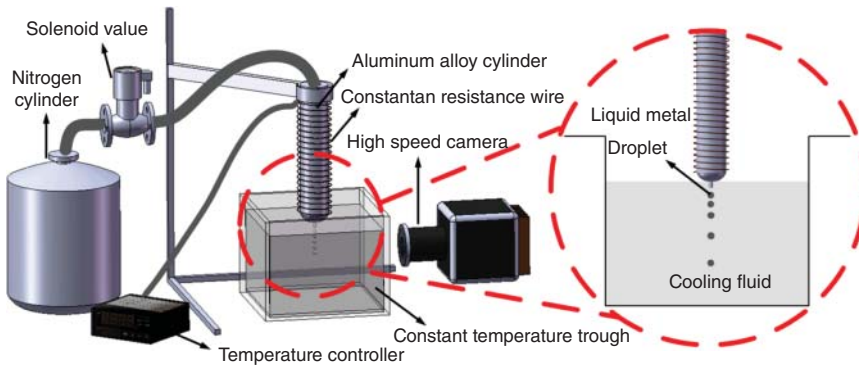


Figure 11.7 Scheme and device for liquid-phase 3D printing toward quick metal fabrication. (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

Table 11.3 The physical properties of the printing ink $\text{Bi}_{35}\text{In}_{48.6}\text{Sn}_{16}\text{Zn}_{0.4}$ [30].

Density (g cm^{-3})	Melting point ($^{\circ}\text{C}$)	Supercooling degree ($^{\circ}\text{C}$)	Melting enthalpy (J g^{-1})	Specific heat capacity ($\text{J g}^{-1} ^{\circ}\text{C}^{-1}$)
7.898	58.3	2.4	28.94	0.262 at $25 ^{\circ}\text{C}$

physical properties are presented in Table 11.3. The metal ink is filled in a syringe. And the syringe is installed in an aluminum alloy cylinder, which is wrapped with constantan resistance wire ($62 \Omega \text{ m}^{-1}$). As the resistance wire is electrified, the Joule heating effect is generated and the temperature of aluminum alloy cylinder, the syringe, and the metal ink is thus increased. The temperature is maintained at a certain value by a temperature controller, which could adjust the current passing through the resistance wire. In order to provide constant driving pressure on the metal ink, a nitrogen cylinder is connected to the syringe and the pressure on the ink is regulated through a solenoid valve. The syringe capillary needle is immersed in the cooling fluid to ensure that the fluid could be in direct contact with the liquid metal droplet upon its formation. The temperature of the cooling fluid should be lower than that of the metal ink to enable cooling of the liquid metal droplet. The formation and the dropping processes are captured by a high-speed camera (Nikon NR-S3) with 30 frames per second and exposure time 1.999 s.

11.3.2 Forming Principle of Metal Objects in Cooling Liquid

The formation and deposition of the droplet is the key issue in the liquid-phase 3D printing method. The whole process of the droplet formation is presented in Figure 11.8. When the average falling speed of the droplet is small (3.34 mm s^{-1}), a large spherical droplet will be formed at the tip of the needle (as shown in Figure 11.8A) due to the large surface tension between the liquid metal and the cooling fluid. With the increase in the falling speed, adjacent droplets get

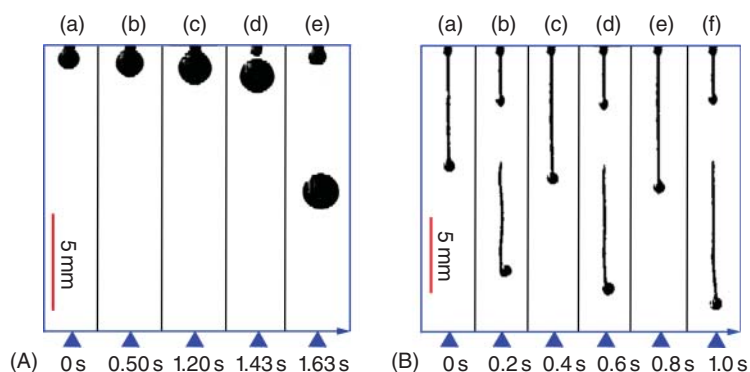


Figure 11.8 Dynamic droplet configurations in liquid-phase fluid: (A) the droplet formation process in water (the droplet falling velocity is 3.34 mm s^{-1}); (B) the long tail tadpole-like droplets due to fast injection speed in ethanol cooling fluid (the droplet falling velocity is 7.98 mm s^{-1}). (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

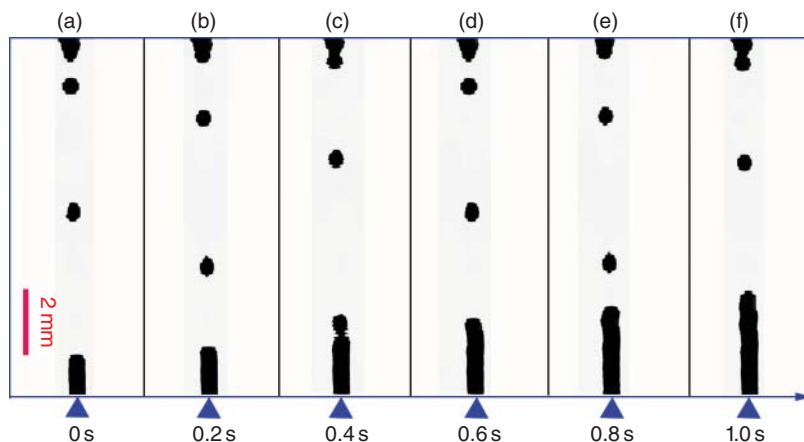


Figure 11.9 The droplet deposition process (from a to f) in ethanol cooling fluid (the droplet falling velocity is 5.65 mm s^{-1}). (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

closer and closer until they contact each other. Consequently, a series of liquid metal tadpoles with long tail outflow the needle successively, which is shown in Figure 11.8B.

Take the printing of a metal column as an example to illustrate the deposition process presented in Figure 11.9. As a molten droplet falls onto the printed column, the top of the column absorbs the heat and fuses with the droplet. The column gradually grows into the desired metallic structure.

11.3.3 Liquid-Phase Printing of Metal Structures

Several different metal structures printed by liquid-phase printing method are shown in Figure 11.10. The metal balls shown in Figure 11.10a are fabricated

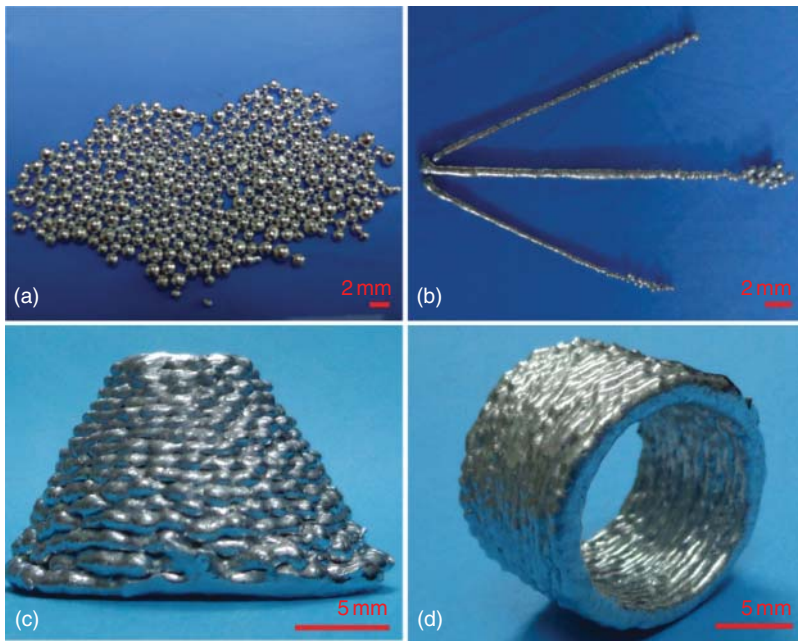


Figure 11.10 Typical 3D metal structures made by liquid-phase 3D printing method. (a) Metal balls; (b) metal rods; (c) frustum of a cone structure; and (d) cylinder structure. (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

by injecting the liquid metal ink through the needle of 0.26 mm inner diameter into ethanol cooling fluid at room temperature. Such a printing method provides a convenient way for mass-manufacturing of solid tin balls, which could find application in electronics industry. Several metal rods printed along the vertical direction are presented in Figure 11.10b. They are hard to be realized through the traditional air cooling or sand cooling methods. Besides, 3D structures such as circular truncated cones and circular rings can also be printed by liquid-phase printing method. The fabrication process is as follows: First, a 3D model of the real object is created with a computer-aided design software (such as SolidWorks) and the file is saved as *.stl format and imported into a slicing software (such as Slic3r [31]). Then, the model is sliced into a set of horizontal layers and a toolpath is generated for each layer. The printing head is controlled along the toolpaths and the 3D structure is finally shaped through liquid metal deposition layer by layer in the cooling fluid.

11.3.4 Factors Affecting the Printing Quality

There are several factors affecting the printing quality when using liquid-phase 3D printing method. The property of the cooling fluid has a significant influence on the printing effect. If the temperature of the cooling fluid is set too high, the falling droplet cannot be instantly solidified and the printed part cannot realize rapid prototyping. Only when it is lower than the melting point of the metal ink, can the falling droplets be solidified. But if the temperature of the cooling fluid

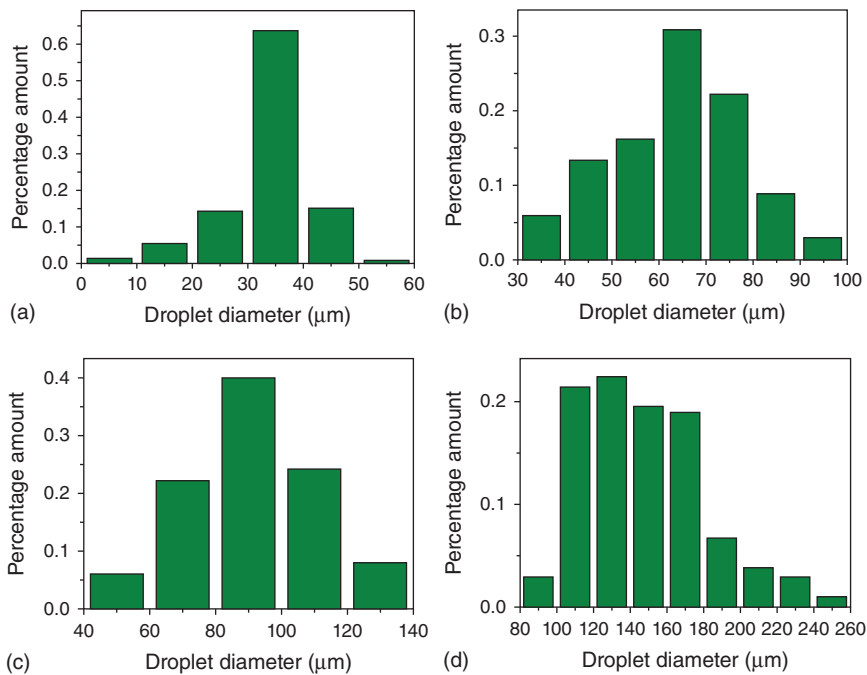


Figure 11.11 The size distribution of the droplets produced with syringe needles of 0.16 mm (a), 0.34 mm (b), 0.51 mm (c), and 0.84 mm (d) inner diameters, respectively. (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

is very low, the falling molten droplets will be transformed into solid particles in short time and the formed metal structure is difficult to “grow”. Besides, the viscosity of the cooling fluid will affect the resistance of the falling droplets and further influence the falling time. And the cooling fluid density will affect the buoyancy of the droplets.

To the pneumatic type fused deposition modeling with liquid-phase cooling method, the air pressure exerted on the liquid metal ink and the inner diameter of the capillary needle directly affect the size and the falling speed of the generated droplets. Figure 11.11 presents the statistical size distribution of the droplets formed by using needles of different sizes. All the experiments are carried out with the ethanol cooling fluid at room temperature. With the increase of the needle inner diameter, the size of the generated droplets exhibits an increasing tendency. As the inner diameters of the syringe needles are respectively 0.16, 0.34, 0.51, and 0.84 mm, the diameter ranges of the generated droplets are 30–40, 60–80, 80–100, and 100–180 μm, respectively.

11.3.5 Comparison Between Liquid-Phase Cooling and Gas-Phase Cooling

Compared to the conventional gas-phase cooling method, liquid-phase cooling owns the merit of rapid prototyping. Figure 11.12a shows a metal rod produced by the liquid-phase printing method, while Figure 11.12b shows a molten globule by the gas-phase cooling method. The large difference in the properties of the

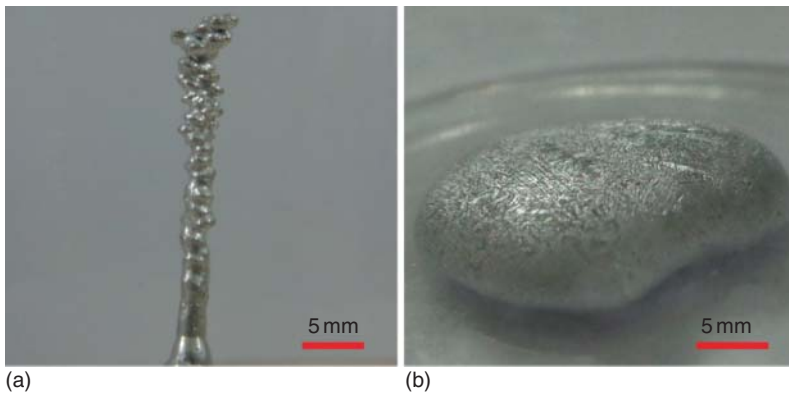


Figure 11.12 Comparison between ethanol cooling and air cooling printings: (a) column formed by the ethanol cooling method; (b) molten globule formed by the air cooling approach. (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

liquid-phase and gas-phase cooling fluids is responsible for this totally different printing effect. In addition to rapid prototyping, liquid-phase printing method owns the advantage of less metal oxidation compared to gas-phase printing, which can be seen from Figure 11.12a.

Table 11.4 comparatively lists the properties of water, ethanol, and dry air, which include thermal conductivity, density, viscosity, and heat capacity. The densities of water and ethanol are, respectively, 828.22 and 655.02, larger than that of dry air. According to the Archimedes principle, which states that the buoyancy force exerted on a body submersed in a fluid equals the weight of the displaced fluid, for a metal droplet, the formula can be expressed as follows:

$$F_{\text{droplet}} = G_{\text{fluid}} = \rho_{\text{fluid}} \cdot g \cdot V_{\text{droplet}} \quad (11.1)$$

where F_{droplet} represents the buoyancy force exerted on the droplet; G_{fluid} and ρ_{fluid} are, respectively, the gravity and the density of the fluid; V_{droplet} is the volume of the droplet; g is the gravitational acceleration constant. Therefore, the buoyancy

Table 11.4 Properties of water, ethanol, and dry air at 100 kPa, 20 °C [30].

Property	Liquid-phase cooling fluid		Gas-phase cooling fluid
	Water	Ethanol	Dry air
Thermal conductivity (λ , W m ⁻¹ K ⁻¹)	0.597	0.24	2.59×10^{-2}
$\lambda/\lambda_{\text{air}}$	23.05	9.27	1.00
Density (ρ , kg m ⁻³)	0.998	0.7893	1.205
ρ/ρ_{air}	828.22	655.02	1.00
Viscosity (η , Pa s)	0.001	0.0012	17.9×10^{-6}
η/η_{air}	55.87	67.04	1.00
Heat capacity (c , kJ kg ⁻¹ K ⁻¹)	4.1818	2.42	1.005
c/c_{air}	4.16	2.41	1.00

of a liquid metal droplet immersed in water and ethanol are, respectively, 828.22 and 655.02 times larger than that of gas-phase cooling case. The relative thermal conductivities of water and ethanol are, respectively, 23.05 and 9.27 times larger than that of dry air. And this enables the molten metal droplets to have much higher heat transfer rate in liquid-phase cooling fluid. Besides, the relative heat capacities of water and ethanol are, respectively, 4.16 and 2.41 times larger than that of dry air. All these superior thermal performances of liquid-phase fluid enable it to have higher cooling rate compared to the gas-phase fluid.

11.3.6 Vision of the Future Liquid-Phase Printing

Here, a further prospect for future liquid-phase printer is given. Clearly, the ink should be many more low melting point (e.g., higher than room temperature and lower than 300°C) metals, which will not be limited to gallium-based, indium-based, or bismuth-based alloys. It can also be the mixture of these alloys and high melting point metal nanoparticles with excellent conductive or mechanical property to obtain higher physical performance. The temperature of the cooling fluid should be lower than the melting point of the metal ink. To improve the printing efficiency, syringe pump array and capillary needle array as shown in Figure 11.13 should be taken into consideration when designing the liquid-phase printer. Such a syringe pump array can be used to extract the liquid metal ink, while the needle array is used to inject the molten metal ink and all the needles can be controlled to turn on and off according to the demand. In

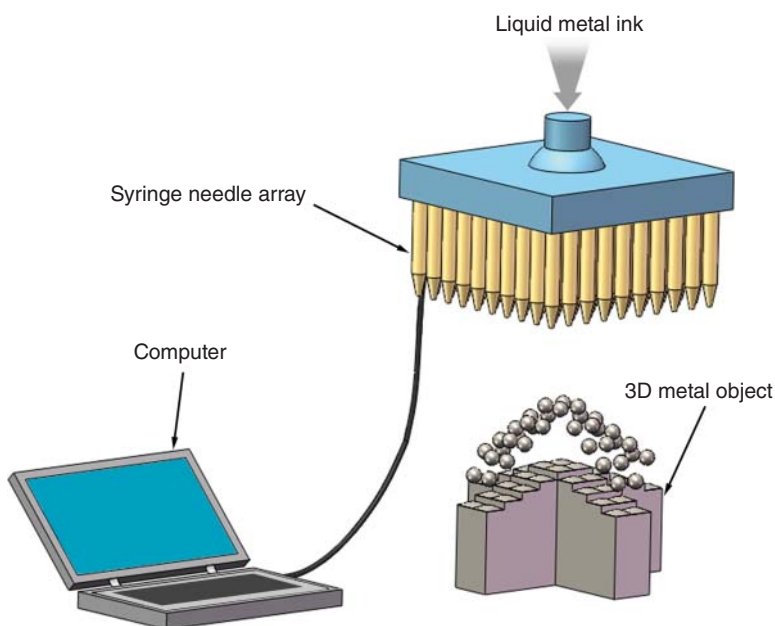


Figure 11.13 Injection needle array for future parallel liquid-phase 3D printer. (Wang and Liu (2014) [30]. Reproduced with permission of Springer.)

this way, a parallel rapid 3D printing of metal structure can be achieved in a moment. This would significantly extend wide adoption of the metal 3D printing into rather complex applications.

Acknowledgment

Several researches as introduced in this chapter were partially supported by the Dean's Research Funding of the Chinese Academy of Sciences and Beijing Municipal Science and Technology Funding (Under Grant No. Z151100003715002) as well as Key Project Funding of Chinese Academy of Sciences.

References

- 1 Lopes, A.J., MacDonald, E., and Wicker, R.B. (2012) Integrating stereolithography and direct print technologies for 3D structural electronics fabrication. *Rapid Prototyping J*, **18**, 129–143.
- 2 Symes, M.D., Kitson, P.J., Yan, J., Richmond, C.J., Cooper, G.J.T., Bowman, R.W., Vilbrandt, T., and Cronin, L. (2012) Integrated 3D-printed reactionware for chemical synthesis and analysis. *Nat. Chem.*, **4** (5), 349–354.
- 3 Griffith, L.G. and Naughton, G. (2002) Tissue engineering-Current challenges and expanding opportunities. *Science*, **295** (5557), 1009–1014.
- 4 Seyednejad, H., Gawlitta, D., Dhert, W.J.A., van Nostrum, C.F., Vermonden, T., and Hennink, W.E. (2011) Preparation and characterization of a three-dimensional printed scaffold based on a functionalized polyester for bone tissue engineering applications. *Acta Biomater.*, **7** (5), 1999–2006.
- 5 Therriault, D., White, S.R., and Lewis, J.A. (2003) Chaotic mixing in three-dimensional microvascular networks fabricated by direct-write assembly. *Nat. Mater.*, **2** (4), 265–271.
- 6 Gu, D.D., Meiners, W., Wissenbach, K., and Poprawe, R. (2012) Laser additive manufacturing of metallic components: Materials, processes and mechanisms. *Int. Mater. Rev.*, **57** (3), 133–164.
- 7 Asgharzadeh, H. and Simchi, A. (2005) Effect of sintering atmosphere and carbon content on the densification and microstructure of laser-sintered M2 high-speed steel powder. *Mater. Sci. Eng., A*, **403** (1–2), 290–298.
- 8 Santos, E.C., Shiomi, M., Osakada, K., and Laoui, T. (2006) Rapid manufacturing of metal components by laser forming. *Int. J. Mach. Tool. Manu.*, **46** (12–13), 1459–1468.
- 9 Zheng, Y., Zhang, Q., and Liu, J. (2013) Pervasive liquid metal based direct writing electronics with roller-ball pen. *AIP Adv.*, **3** (11), 112117.
- 10 Zheng, Y., He, Z.Z., Yang, J., and Liu, J. (2014) Personal electronics printing via tapping mode composite liquid metal ink delivery and adhesion mechanism. *Sci. Rep.*, **4**, 4588.
- 11 Zhang, Q., Gao, Y.X., and Liu, J. (2014) Atomized spraying of liquid metal droplets on desired substrate surfaces as a generalized way for ubiquitous printed electronics. *Appl. Phys. A: Mater. Sci. Process.*, **116** (3), 1091–1097.

- 12 Jin, C., Zhang, J., Li, X.K., Yang, X.Y., Li, J.J., and Liu, J. (2013) Injectable 3-D fabrication of medical electronics at the target biological tissues. *Sci. Rep.*, **3**, 34.
- 13 Kramer, R.K., Majidi, C., and Wood, R.J. (2013) Masked deposition of gallium-indium alloys for liquid-embedded elastomer conductors. *Adv. Funct. Mater.*, **23** (42), 5292–5296.
- 14 Fassler, A. and Majidi, C. (2013) 3D structures of liquid-phase GaIn alloy embedded in PDMS with freeze casting. *Lab Chip*, **13** (22), 4442–4450.
- 15 Sostman, H.E. (1977) Melting point of gallium as a temperature calibration standard. *Rev. Sci. Instrum.*, **48** (2), 127–130.
- 16 Assael, M.J., Armyra, I.J., Brillo, J., Stankus, S.V., Wu, J.T., and Wakeham, W.A. (2012) Reference data for the density and viscosity of liquid cadmium, cobalt, gallium, indium, mercury, silicon, thallium, and zinc. *J. Phys. Chem. Ref. Data*, **41** (3), 033101.
- 17 Alchagirov, B.B. and Mozgovoi, A.G. (2005) The surface tension of molten gallium at high temperatures. *High Temp.*, **43** (5), 791–792.
- 18 Regan, M.J., Tostmann, H., Pershan, P.S., Magnussen, O.M., DiMasi, E., Ocko, B.M., and Deutsch, M. (1997) X-ray study of the oxidation of liquid-gallium surfaces. *Phys. Rev. B*, **55** (16), 10786–10790.
- 19 Wang, L. and Liu, J. (2013) Liquid metal material genome: Initiation of a new research track towards discovery of advanced energy materials. *Front. Energy*, **7** (3), 317–332.
- 20 Zhang, Q. and Liu, J. (2013) Nano liquid metal as an emerging functional material in energy management, conversion and storage. *Nano Energy*, **2** (5), 863–872.
- 21 Yi, L.T., Jin, C., Wang, L., and Liu, J. (2014) Liquid-solid phase transition alloy as reversible and rapid molding bone cement. *Biomaterials*, **35** (37), 9789–9801.
- 22 Maxwell, J.C. (1904) *A Treatise on Electricity and Magnetism*, Oxford University Press, Cambridge.
- 23 Lu, S.Y. and Lin, H.C. (1996) Effective conductivity of composites containing aligned spheroidal inclusions of finite conductivity. *J. Appl. Phys.*, **79** (9), 6761–6769.
- 24 Wang, B.X., Zhou, L.P., and Peng, X.F. (2003) A fractal model for predicting the effective thermal conductivity of liquid with suspension of nanoparticles. *Int. J. Heat Mass Transfer*, **46** (14), 2665–2672.
- 25 Ma, K.Q. and Liu, J. (2007) Nano liquid-metal fluid as ultimate coolant. *Phys. Lett. A*, **361** (3), 252–256.
- 26 Toth, L.S. and Gu, C.F. (2014) Ultrafine-grain metals by severe plastic deformation. *Mater. Charact.*, **92**, 1–14.
- 27 Matin, A., Saniee, F.F., and Abedi, H.R. (2015) Microstructure and mechanical properties of Mg/SiC and AZ80/SiC nano-composites fabricated through stir casting method. *Mater. Sci. Eng., A*, **625**, 81–88.
- 28 Rikhtegar, F., Shabestari, S.G., and Saghafian, H. (2015) The homogenizing of carbon nanotube dispersion in aluminium matrix nanocomposite using flake powder metallurgy and ball milling methods. *Powder Technol.*, **280**, 26–34.

- 29 Salleh, M.A.A.M., McDonald, S.D., Terada, Y., Yasuda, H., and Nogita, K. (2015) Development of a microwave sintered TiO_2 reinforced Sn-0.7wt%Cu-0.05wt%Ni alloy. *Mater. Des.*, **82**, 136–147.
- 30 Wang, L. and Liu, J. (2014) Liquid phase 3D printing for quickly manufacturing conductive metal objects with low melting point alloy ink. *Sci. China: Technol. Sci.*, **57** (9), 1721–1728.
- 31 <http://slic3r.org> (19 October 2012)

12

Inkjet Printing of Conducting Polymer Nanomaterials

Edward Song and Jin-Woo Choi

12.1 Introduction

Inkjet printing is a well-established patterning technique commonly used in printing documents on paper or polymer films. However, due to many of its advantages, an inkjet printing technology is being utilized in other applications such as thin-film transistors (TFT), organic electronics, tissue engineering, flexible and wearable devices, and disposable sensors. The main advantages of using the inkjet printer for such device fabrication is the simplicity and the cost effectiveness compared to other fabrication methods such as photolithography. In addition, it offers fully automated process with mass producibility and therefore is a highly attractive technique from a manufacturing perspective. Furthermore, due to the so-called “direct-writing” method enabled by the movement of the ink cartridge and the printer stage, it minimizes wasting of the ink compared to the other top-down patterning approaches [1, 2].

It is well known that numerous types of nanomaterials (nanowires, nanotubes, nanoparticles, etc.) offer many benefits especially in sensing applications where various sensing performance criteria such as sensitivity, limit of detection, response time, and selectivity were reported to have been significantly improved [3]. Therefore, patterning of such nanomaterials on a thin substrate is a topic of great interest from the perspective of printable low-cost sensor development. Many different types of nanomaterials such as carbon nanotubes, nanoparticles, graphene sheets, and polymer nanomaterials have been patterned on either paper or polymer films using inkjet printing methods to develop working devices. Some examples include biosensors, gas sensors, RFID tags, energy storage devices, to name a few.

Conducting polymer is a class of polymers with unique properties. It combines the benefits of a metallic electrical conductivity, a flexible nature of polymeric materials, as well as the high surface-area-to-volume ratio when it is in the form of nanomaterials. Moreover, the synthesis of the conducting polymer nanomaterials is relatively facile and inexpensive compared to other metal- or semiconductor-based nanomaterials. Hence, inkjet printing of conducting polymer nanomaterials can be widely utilized in flexible and wearable electronics as well as in printable sensors.

This chapter focuses on the most recent developments in inkjet printing of conducting polymer nanomaterials. The aim of this effort is to elucidate this subject to the readers with a broad range of topics including inkjet-based patterning resolution, strategies to disperse and suspend conducting polymer nanomaterials in liquid, sensing performances of the devices fabricated by inkjet printing, and other applications that utilize inkjet printing of conducting polymer nanomaterials.

12.2 Inkjet Printing of Polyaniline Nanomaterials

12.2.1 Introduction

Polyaniline has been reported to be the oldest known intrinsically conducting polymer [4] as well as one of the most widely studied conducting polymers available. Its unique material properties have been extensively studied [5–8], which make it amenable to a wide range of applications. Some examples of polyaniline's unique characteristics are highly conductive under acidic environment, relatively simple doping and dedoping process, color change depending on its oxidation state, and a natural tendency to be synthesized in a one-dimensional nanowire shape [9]. Before delving into the details of inkjet printing of polyaniline, a brief overview on the chemical, electrochemical, and electrical properties as well as the synthesis of polyaniline is presented in this section.

12.2.2 Chemical Structure, Electrochemical Properties, and Conductivity of Polyaniline

A general chemical structure of polyaniline consists of a series of benzene rings connected in *para*-positions (connected in the 1 and 4 positions of the aromatic compounds) with either an amine or imine nitrogen atom positioned between the rings as shown in Figure 12.1 [5]. The proportions of the amine and imine nitrogen atoms present in polymer structure determine the oxidation state of polyaniline, namely fully reduced (i.e., leucoemeraldine) if only amine nitrogen atoms are present and fully oxidized (i.e., pernigraniline) if only imine nitrogen atoms are present. Polyaniline can also exist in the partially oxidized form where both amine and imine groups coexist in the same polymer chain. Polyaniline

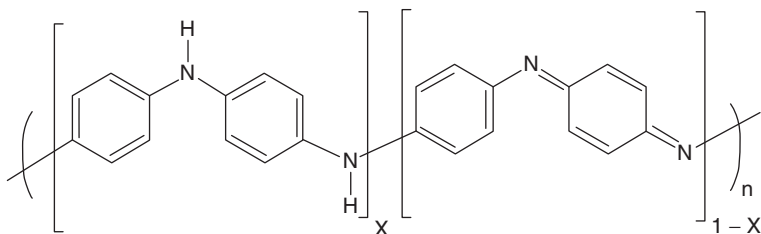


Figure 12.1 A general chemical structure of polyaniline consisting of amine repeating units and imine repeating units.

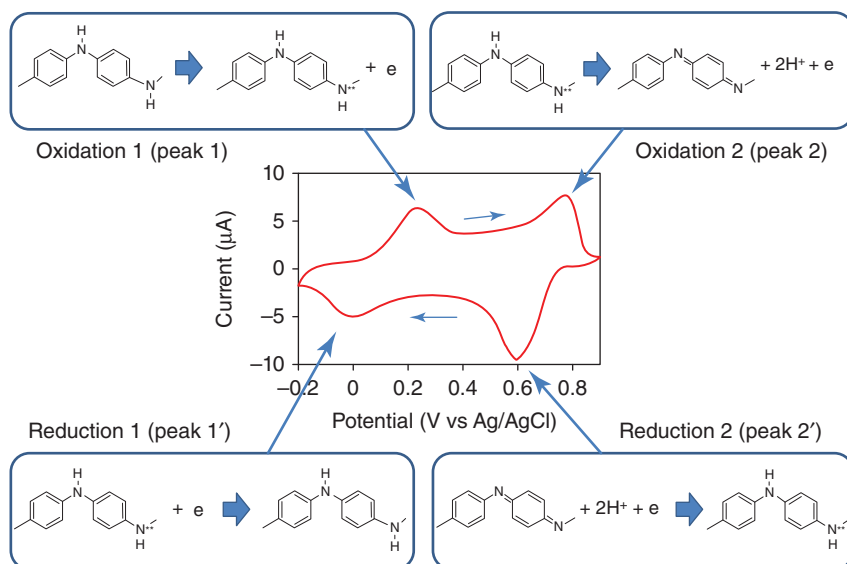


Figure 12.2 A typical cyclic voltammetry curve of polyaniline under acidic media (pH 1) with a description of the redox reaction occurring at each oxidation or reduction peak. (Song and Choi (2013) <http://www.mdpi.com/2079-4991/3/3/498/htm>.)

is known to exhibit maximum electrical conductivity when it is approximately half-oxidized (i.e., emeraldine), whereas it is nearly insulating when it is either fully oxidized or fully reduced [10, 11]. Hence, its oxidation state plays a critical role in determining its conductivity.

Cyclic voltammetry (CV) is an effective tool for studying the electrochemical properties of many materials, and hence it is often used to examine the redox chemistry of polyaniline [12]. A typical CV plot of polyaniline is shown in Figure 12.2, where two distinct sets of redox couples are present in the graph. The oxidation and reduction peaks in the CV plot refer to the corresponding transition of the polyaniline from one state to another. For example, the oxidation peaks 1 and 2 correspond to the transformation of polyaniline from leucoemeraldine to emeraldine and emeraldine to pernigraniline, respectively. Conversely, the reduction peaks 1' and 2' correspond to the opposite transformation of the polyaniline in terms of its redox state.

The electrical conductivity of polyaniline is primarily influenced by two factors: the oxidation state of the polymer and the level of protonation also known as doping. In polyaniline, the main charge carriers responsible for electronic conduction are the holes, which are delocalized radical cations, generated within the polymer chain as a result of proton-doping process [8]. The chemical structure of polyaniline indicates that both fully oxidized (pernigraniline) and fully reduced (leucoemeraldine) forms of polyaniline contain no moving charge carriers; therefore, they are both electrically insulating even if it is doped with protons. However, it turns out that polyaniline exhibits maximum conductivity when it is approximately half-oxidized in its emeraldine form. Moreover, since

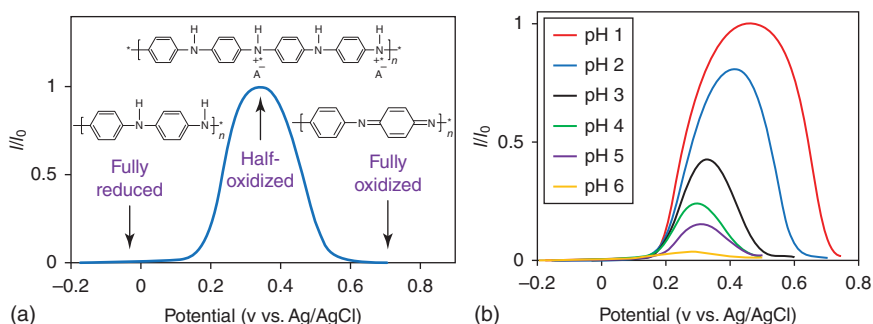


Figure 12.3 The relationship between conductivity, oxidation state, and the protonation level of polyaniline: (a) the normalized conductance current versus electrochemical potential and (b) the same plot under pH 1–6 buffer solutions.

protonation is required for polyaniline to be conductive, it must be exposed to the acidic media: the stronger the acidity, the higher the conductivity. The relationship between the electrical conductivity, oxidation state, and the protonation level of polyaniline is summarized in Figure 12.3.

One major drawback of polyaniline is its complete loss of conductivity at neutral or base environment. This is of significant concern if polyaniline is to be used in biosensor applications where most biological molecules and enzymes are active only in neutral solutions of pH typically ranging from 6 to 8. Many efforts have been directed toward improving the conductivity of polyaniline at neutral and at even higher pH environment. Some of the most successful techniques include self-doping of polyaniline [13, 14], copolymerization with ring-substituted aniline derivatives, and incorporation of high-molecular-weight anions such as camphorsulfonic acid (CSA) [15–17], dodecylbenzenesulfonic acid (DBSA) [18, 19], polyacrylic acid (PAA) [20, 21], and polystyrene sulfonate (PSS) [22, 23]. Other remaining challenges regarding polyaniline that require further attention are conductivity degradation over time due to the inherent irreversible oxidation [24, 25] and the hysteresis effect of the conductivity of polyaniline [26, 27].

The two most commonly used methods of polyaniline synthesis are electrochemical polymerization and chemical oxidative polymerization. In the electrochemical methods, the polyaniline grows directly on the surface of the electrode of the electrochemical cell, while in the chemical oxidation method, the synthesized polymer is suspended in liquid phase. Therefore, as far as the printability of the polyaniline nanomaterials is concerned, the chemical synthesis method is the preferred method of growth for inkjet printing applications. Nanofibers (or nanowires) and nanoparticles are the two commonly synthesized nanostructures of polyaniline. The synthesis of polyaniline nanofibers was pioneered by Kaner (and Manohar) [28, 29], where highly directional nanofibers were produced by two different methods: interfacial polymerization technique [28, 30] and rapid mixing technique [31, 32]. The synthesis of polyaniline nanoparticles is typically done by the oxidation of aniline monomers in the presence of polymeric

stabilizers such as DBSA, polyvinyl alcohol (PVA), and poly-*N*-vinylpyrrolidone resulting in a granular and nanoparticle-like morphology.

12.2.3 Inkjet-Printed Polyaniline Nanomaterials

To the best of our knowledge, the earliest reporting on the inkjet printing of polyaniline nanomaterials are in [33, 34] where nanoparticles with an average diameter of a few tens of nanometers were chemically synthesized and inkjet-printed using a piezoelectric-based printer. It was thought that nanowires of a few micrometers in length may not be suitable for inkjet printing due to the possibility of clogging that may arise during the patterning process. However, it was recently demonstrated that polyaniline nanowires can also be printed with minimum clogging of the printhead [35] given the fact that a typical nozzle size of inkjet printers is on the order of tens of micrometers [36]. Figure 12.4 shows the interconnected morphology of polyaniline nanofibers after synthesis and after inkjet printing [35].

The minimum resolution that is easily achievable using a low-cost, commercially available inkjet printer is approximately 150–200 μm , and this resolution is maintained even if multiple layers are printed on the same location [35]. Therefore, this method can be used to fabricate low-cost printable electronic devices. Figure 12.5 shows the patterning ability of inkjet-printed polyaniline materials with varying line width and spacing.

The use of thermally actuated inkjet printers was initially avoided and the piezoelectric printers were preferred due to the concern that elevated heat (typically around 300 $^{\circ}\text{C}$ [37]) may have detrimental effect on conducting polymers and biomaterials such as enzymes (horse radish peroxidase (HRP), glucose oxidase (GOx), etc.). However, it was reported that the conductivity of polyaniline nanowires was minimally affected by the heat generated by the printer nozzles [37]. Furthermore, biological materials have been successfully inkjet-printed without significant reduction in their activity [38]. Various shapes of polyaniline nanomaterials have been inkjet-printed on a substrate, including nanowires [35] and nanoparticles [33]. Inkjet printing of polyaniline nanoparticles having the

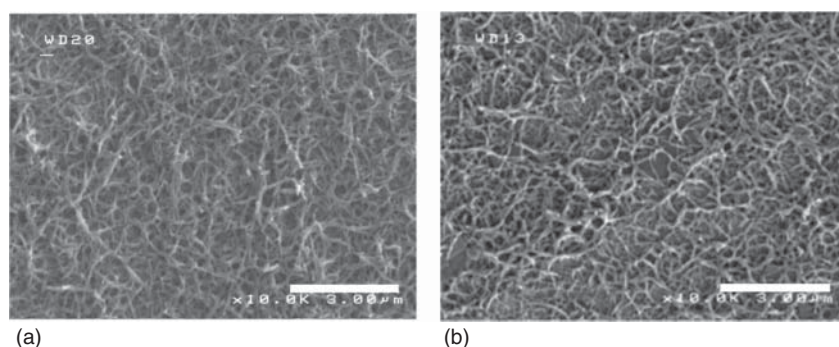


Figure 12.4 The scanning electron microscope (SEM) image of the polyaniline nanowires (a) as-synthesized and (b) after inkjet printing on a transparency film (five prints). (Song *et al.* (2015) [35]. Reproduced with permission of Elsevier.)

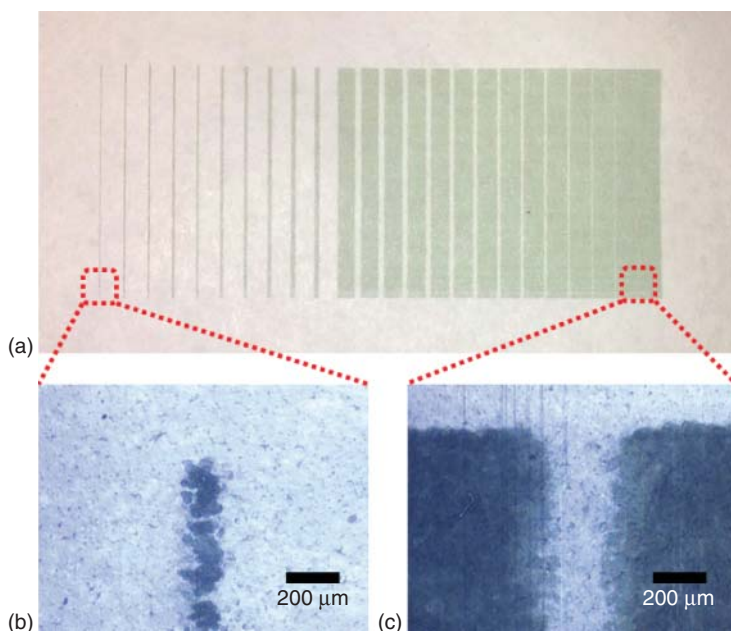


Figure 12.5 Minimum line and gap width achievable with inkjet patterning of polyaniline nanowire network (printed five times). (Song *et al.* (2015) [35]. Reproduced with permission of Elsevier.)

average particle size of 65 nm in diameter on a PET substrate has been reported [33], and this technique was used to fabricate various printable devices and sensors. A piezoelectric printer was commonly used since it does not require heating of the ink; however, studies on a thermally actuated inkjet printer demonstrated that the heating of the polymer had negligible effect either on the conductivity or on the morphology of the polyaniline nanomaterials [35, 37].

One of the major challenges with the inkjet printing of polyaniline nanomaterials is the development of a well-dispersed polyaniline nanoparticles suspended in aqueous solution. Jang *et al.* have synthesized polyaniline nanoparticles in the presence of polystyrenesulfonate (PSS) to produce polyaniline-poly (4-styrenesulfonate) (PANI-PSS) nanoparticles, which, due to the strong electrostatic interactions, remain well-suspended in liquid for an extended period of time [34]. Other commonly used surfactants that help the dispersion of nanomaterials in liquid include SDS, PVP, and DBSA.

Another factor to consider when inkjet printing polymer materials is to ensure that the right viscosity and surface tension of the ink are achieved [34]. *N*-Methyl-2-pyrrolidone (NMP) combined with ethylene glycol and isopropyl alcohol in an aqueous base solution is known to be effective in producing consistent printing results [37].

12.2.4 Applications of Inkjet-Printed Polyaniline Nanomaterials

Due to its ease of deposition and patterning of nanomaterials, one of the immediate applications of this technique is the fabrication of a printable sensor. The

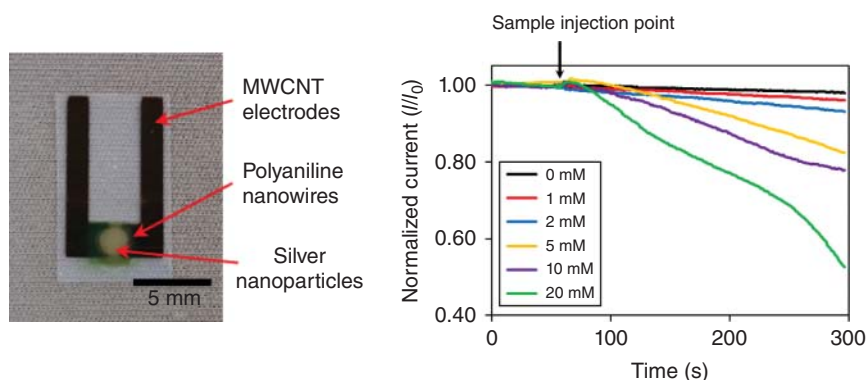


Figure 12.6 A chemiresistive hydrogen peroxide sensor: (a) image of the sensor showing printed polyaniline nanowire network modified with catalytic silver nanoparticles and (b) the conduction current response of the sensor when exposed to various concentrations of H_2O_2 . (Song *et al.* (2015) [35]. Reproduced with permission of Elsevier.)

conductivity of polyaniline is known to be affected by the exposure to several gas species that cause either doping or dedoping of polyaniline, and, therefore, chemiresistive gas sensors based on polyaniline material have been reported earlier [39]. An inkjet-printed polyaniline nanoparticle-based ammonia sensor was also demonstrated [40], wherein ammonia gas with a concentration of as low as $20\text{ }\mu\text{M}$ was successfully detected. The conductivity of the polyaniline is known to change when it is exposed to ammonia due to the dedoping of protons. They also reported that increasing the print layer thickness resulted in an increased amperometric response to a given ammonia concentration. Moreover, the stability of the printed sensor was monitored over 15 days, which showed minimal fluctuation in the measured current.

Polyaniline nanowire-based chemical sensors fabricated by the inkjet printing technique was demonstrated in [35], where the nanowire network was utilized as a chemiresistive pH sensor and, with the incorporation of catalytic nanoparticles, also as a hydrogen peroxide (H_2O_2) sensor. The formation of the conductive electrodes was achieved by patterning with carbon nanotube ink to demonstrate that the entire sensor can be developed with an inkjet printing method. Figure 12.6 shows an image of the inkjet-printed hydrogen peroxide sensor (left) with its response to various concentrations of H_2O_2 .

12.3 Polypyrrole

12.3.1 Properties and Synthesis of Polypyrrole (Ppy) Nanomaterials

Polypyrrole (Ppy) is another type of material that is widely studied and is considered to be one of the most promising conducting polymers, along with polyaniline. Polypyrrole is known to have excellent thermal and environmental stability and is also relatively simple to synthesize. It also possesses high electrical conductivity often exceeding that of polyaniline, where the highest measured conductivity of polypyrrole was reported to be 288 S cm^{-1} [41]. Ppy nanomaterials

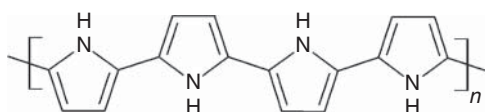


Figure 12.7 A general chemical structure of polypyrrole showing a chain of heterocyclic aromatic compounds.

were often employed for applications in biosensors [42], gas sensors [43], and electrochromic displays [44] among many others.

The general chemical structure of polypyrrole is a linear connection of pyrrole monomers, which are five-membered heterocyclic aromatic compound as shown in Figure 12.7 [45].

Polypyrrole is an electroactive polymer and, therefore, its oxidation states can be controlled by manipulating its electrochemical potential. Figure 12.8 shows a typical cyclic voltammogram of the electrochemically synthesized polypyrrole [46]. Unlike polyaniline, which has two distinct redox reactions, polypyrrole has a single redox couple positioned near -0.2 V versus SCE. When the potential is below -0.4 V versus SCE, polypyrrole remains in a fully neutral state rendering

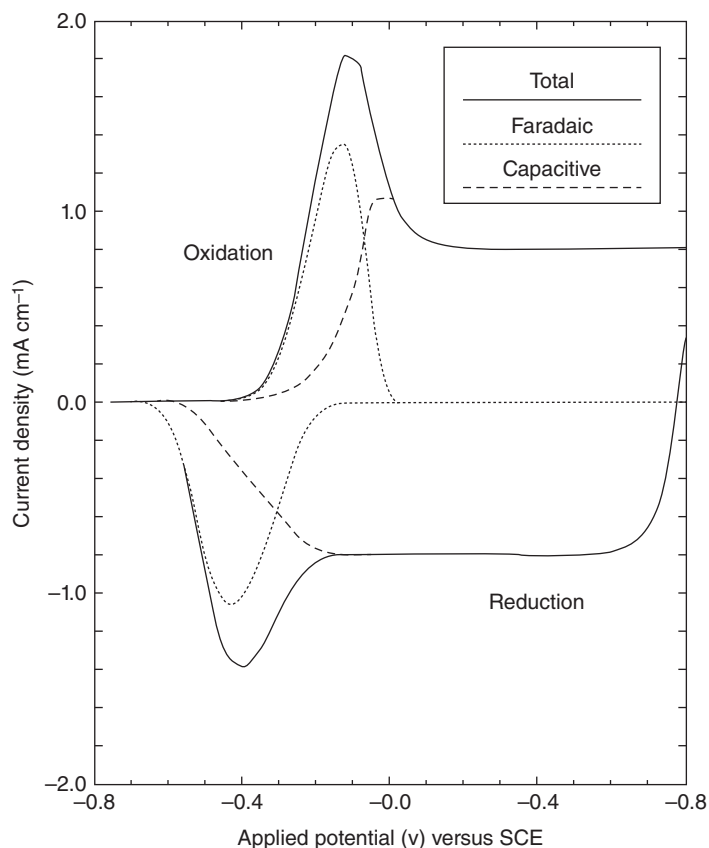


Figure 12.8 Cyclic voltammogram of polypyrrole showing the faradaic and capacitive current components, at a scan rate of 20 mV s^{-1} . (Yeu *et al.* (1991) <http://jes.ecsdl.org/content/138/10/2869.short>.)

it nonconductive. However, as the potential becomes more positive, the polymer begins to be oxidized and as the potential reaches 0.2 V versus SCE, the polymer becomes a fully oxidized and conducting state.

Similar to polyaniline, Ppy can be easily synthesized either by electrochemical polymerization or by chemical synthesis through the oxidation of pyrrole monomers. In electropolymerization, Ppy can be polymerized at a potential of 0.81 V versus saturated calomel electrode (SCE) [45] using an electrochemical cell with an electrolyte containing an appropriate concentration of the pyrrole monomer. Since polypyrrole grows in a randomly oriented manner, the synthesis of polypyrrole with electropolymerization technique results in a uniformly deposited film on the surface of the electrode. The main difference between polyaniline and polypyrrole in terms of their polymerization process is that polyaniline possesses a natural capability to be synthesized in a unidirectional nanofiber morphology, while polypyrrole does not have such a capability and therefore fabrication of polypyrrole nanomaterials is slightly more difficult than polyaniline. In order to produce one-dimensional nanostructures such as nanofibers or nanorods, a structure guiding template is commonly employed. Examples of hard templates include carbon nanotubes and porous membranes [47–49] such as anodized aluminum oxide (AAO) and porous aluminosilicate. Common examples of soft templates are various surfactants [50], organic substances, block copolymers, nucleotides [51, 52], micelles [53], and lipids [54]. Soft-template methods are especially attractive since the templates are easy to remove after the synthesis, whereas the removal of hard templates often requires treatment with harsh chemicals, which could damage the nanomaterials.

Many soft templates have been used for the synthesis of one-dimensional polypyrrole nanomaterials. Many types of surfactants are known to greatly influence the particle size and distribution of the polypyrrole nanoformulations [55]. Long-chain cationic surfactants cetyltrimethylammonium bromide (CTAB) [56, 57] and dodecyltrimethylammonium bromide (DTAB) [50] have been mixed with pyrrole monomers along with ammonium peroxydisulfate (APS) to produce ribbon- and wire-like nanostructures by chemical synthesis. An anionic surfactant sodium dodecylsulfate (SDS) alone was shown to be ineffective in producing one-dimensional morphology. Although APS has been commonly used as a chemical oxidizing agent for the production of polyaniline nanowires, iron(III) chloride (FeCl_3) is a preferred choice of oxidant since polypyrrole prepared with FeCl_3 shows higher conductivity [58]. It is interesting to note that when APS is used as oxidants to synthesize both polyaniline and polypyrrole, the conductivity of polyaniline is generally higher than that of polypyrrole. However, when FeCl_3 is used as oxidants, polypyrrole exhibits higher conductivity than polyaniline. Polypyrrole nanofibers and nanotubes have also been synthesized by the seeding approach where various nanomaterials including single-walled carbon nanotubes (SWCNT) and V_2O_5 nanofibers were used as seed templates as shown in Figure 12.9 [29, 60]. Template-free synthesis method of polypyrrole nanofiber network was also demonstrated [59].

The addition of dopamine (DA), a biological neurotransmitter, has also been reported to promote the fibrous growth of polypyrrole [61]. The optimum synthesis condition that resulted in one-dimensional polypyrrole fibers was the molar

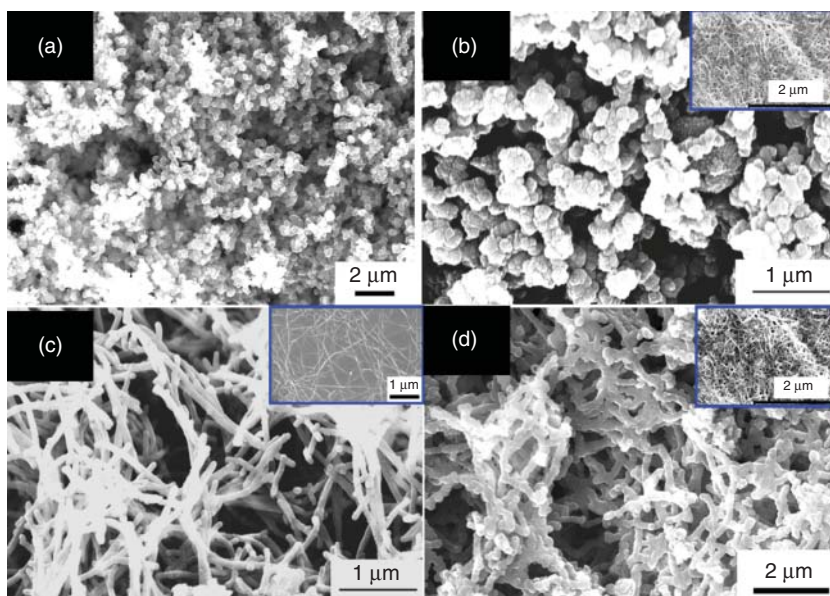


Figure 12.9 SEM images of polypyrrole (insets: seed template): (a) unseeded reaction; (b) seeded with 1.5 mg HiPco SWCNT; (c) seeded with 4 mg of V_2O_5 ; (d) seeded with SWCNT pre-exposed to $(NH_4)_2S_2O_8$. (Zang *et al.* (2008) [59]. Reproduced with permission of American Chemical Society.)

ratio of DA and pyrrole monomer being 0.5. However, the DA functionalized Ppy exhibited the maximum conductivity of 3.8 S cm^{-1} (in pellet form) when the DA/Ppy mole ratio was at 0.1. They found that Ppy nanofibers functionalized with DA not only changed their morphology but also enhanced their adhesion to other surfaces due to the adhesive nature of the self-polymerized polydopamine. Figure 12.10 shows the different morphologies of the Ppy nanomaterials when synthesized with different DA/Ppy mole ratios.

Based on the stoichiometry as illustrated in Figure 12.11 [58], the oxidant-to-molar ratio for the polymerization of both aniline and pyrrole is 1.25, meaning that for every four molecules of either aniline or pyrrole monomers, five molecules of APS oxidant are required to polymerize a chain consisting of four monomers. However, for optimal growth condition for one-direction nanofibers, an oxidant-to-molar ratio of 0.25 was used [9, 28].

Using a significantly smaller concentration of oxidants is believed to help suppress the secondary growth on the already grown nanowires, thereby preserving the one-dimensional morphology. Addition of larger molecules such as dimers or oligomers of the same type has been reported to promote one-dimensional nanostructures since those larger molecules generally have lower oxidation potential and, therefore, serve as growth initiators and seeding materials [9].

12.3.2 Inkjet Printing and Applications of Ppy Nanomaterials

One of the earliest reports on the inkjet-printed polypyrrole patterns is in [62] where a thin film of polypyrrole was deposited on a polyester film to be used as a

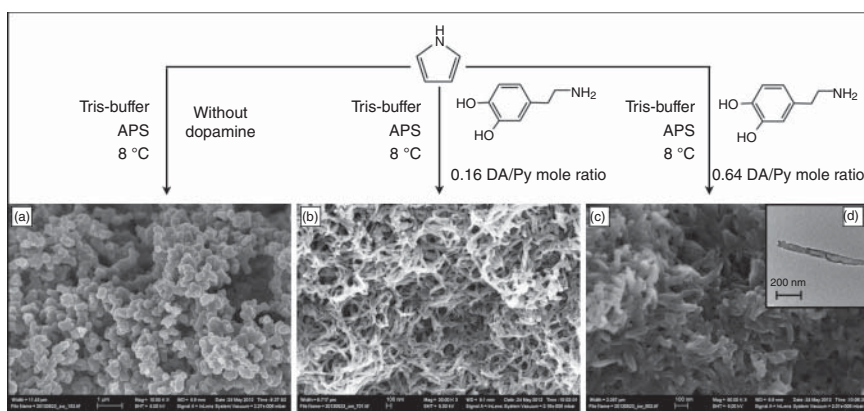


Figure 12.10 SEM images of (a) Ppy with globular shape; (b) fibrous Ppy morphology that resulted from 0.5 DA/Py mole ratio; (c) more compacted fibrous Ppy morphology that resulted from 2 DA/Py mole ratio; and (d) TEM topography image of a single PDA-Ppy fiber that resulted from 2 DA/Py mole ratio. (Mabrook *et al.* (2006) [62]. Reproduced with permission of Elsevier.)

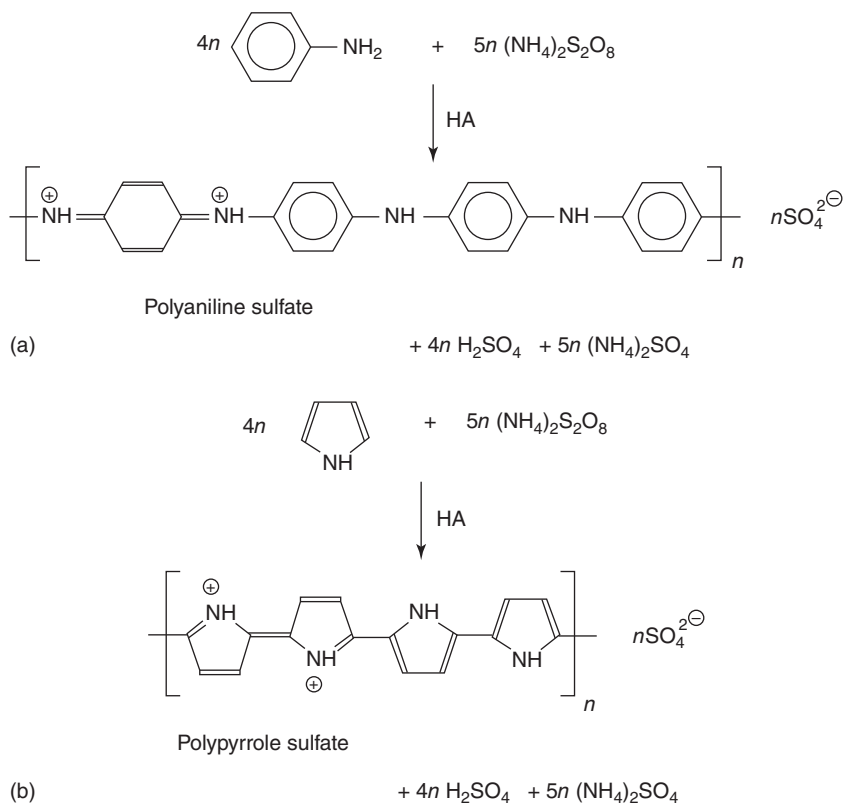


Figure 12.11 The stoichiometry of (a) the oxidation of aniline with APS in acidic aqueous medium yielding protonated polyaniline in its emeraldine form and (b) the oxidation of pyrrole resulting in a protonated polypyrrole.

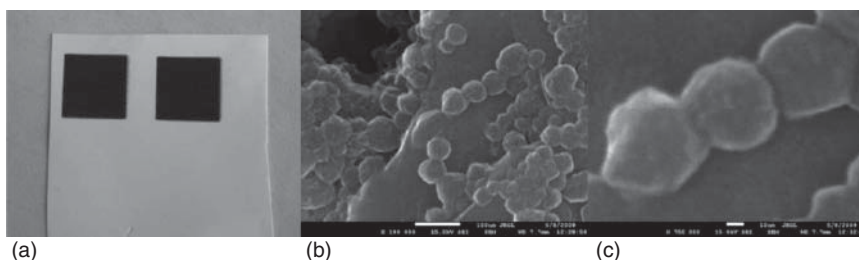


Figure 12.12 Inkjet-printed Ppy/GA formulations. (a) Digital photo of Ppy/GA film printed 20 times on PVDF membrane; (b) SEM image of the printed Ppy/GA particles, scale bar = 100 nm; and (c) magnified SEM image showing the Ppy/GA nanoparticles, scale bar = 10 nm. (Weng *et al.* (2011) [55]. Reproduced with permission of Royal Society of Chemistry.)

resistive gas vapor sensor. Although the deposited polypyrrole materials were not in nanoscale, a uniform film containing interconnected islands with an average diameter of $25\ \mu\text{m}$ were printed on a substrate that is sufficiently small enough to be ejected through the printer nozzle. By measuring the change in resistance, the developed sensor was able to detect various gas molecules including methanol, ethanol, propanol, chloroform, and benzene.

Researchers have also used other types of advanced surfactants such as gemini salt (GS) and acid (GA) to produce a smaller and more uniform polypyrrole particle distribution with an average particle size of 142 nm [55], as shown in Figure 12.12, which was significantly smaller than those synthesized with SDS or sodium dodecyl benzene sulfonate (SDBS). The nanoparticles were then inkjet-printed with a piezoelectric Dimatix Materials Printer (DMP 2800) achieving a minimum line width of $70\ \mu\text{m}$. Due to the nanoscale particle size of the conducting polymers with good dispersion that indicated no sign of agglomeration for an extended time period, no major clogging problems had occurred.

Using GA as surfactants, a highly conductive film with a conductivity of $4.95\ \text{S cm}^{-1}$ was achieved although its viscosity and surface tension were not optimized to be inkjet-printed. With the optimized ink condition, a conductivity of $0.5\ \text{S cm}^{-1}$ was demonstrated.

Wallace *et al.* have used the inkjet printing of Ppy nanoparticle dispersions in conjunction with enzymes, horse radish peroxidase (HRP), and glucose oxidase (GOx) to develop biosensors for the detection of H_2O_2 and glucose [63]. They have confirmed that even after printing the Ppy/enzyme formulations on a PET film the enzymes maintained their activity on the biosensor. For example, the Ppy/HRP formulation had increased the oxidation potential of H_2O_2 to $-0.25\ \text{V}$ versus Ag/AgCl compared to the oxidation potential of $-0.4\ \text{V}$ for Ppy film without the enzyme as shown in Figure 12.13. Moreover, to prevent the water-soluble enzyme molecules from being immobilized away from the sensor, a protective layer of ethyl cellulose in butanol was also coated on top of the sensor with an inkjet printer.

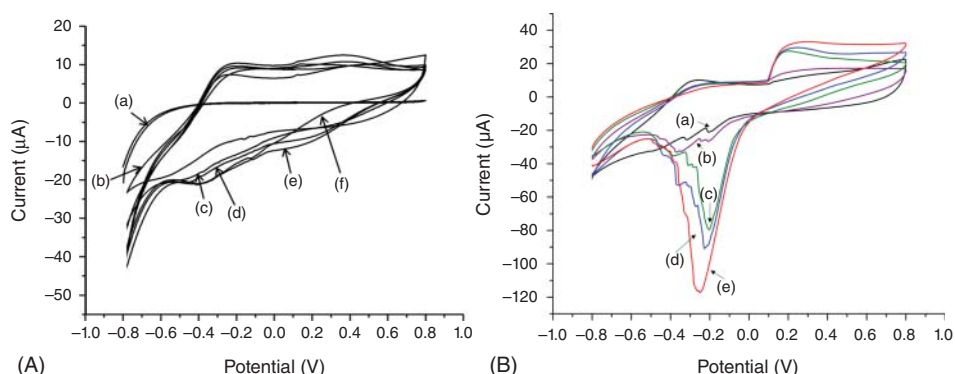


Figure 12.13 (A) CV curves of (a) bare and (b–f) Ppy-modified screen-printed carbon electrodes (SPCEs) in 0.01 M PBS with various H_2O_2 concentrations. In (b–f), the SPCEs were exposed to 0, 1, 10, 100, and $1000 \mu\text{M}$ H_2O_2 , respectively; (B) CV curves of SPCEs modified with inkjet-printed Ppy/HRP in 0.01 M PBS. In (a–e), the electrodes were exposed to 0, 1, 10, 100, and $1000 \mu\text{M}$ H_2O_2 , respectively. HRP loading is 2.5 mg mL^{-1} . All potentials are versus Ag/AgCl (3.0 M NaCl) and the scan rate was 0.1 V s^{-1} . (Weng *et al.* (2012) [64]. Reproduced with permission of Elsevier.)

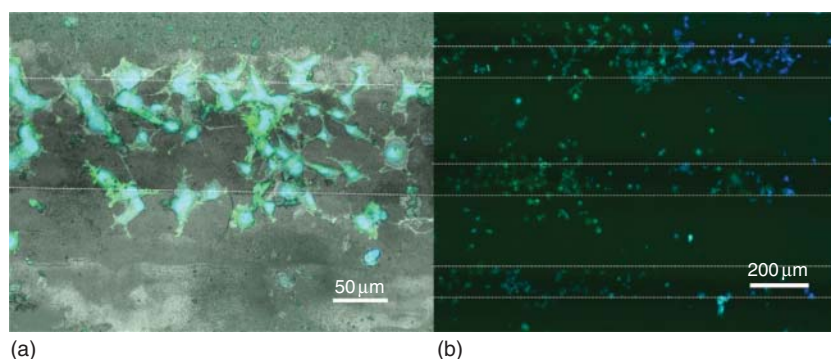


Figure 12.14 (a) Overlap of fluorescence and optical microscopy image of PC12 cells cultured on inkjet-printed Ppy/collagen scaffold; (b) fluorescence microscopy images of PC12 cells cultured on Ppy/collagen scaffold. (Hanawa *et al.* (1989) [65]. Reproduced with permission of Elsevier.)

In another work, they have also implemented a set of electrode lines patterned with Ppy via inkjet printing for application in electrical stimulation of cells [64]. Collagen has also been inkjet-printed on top of the conducting polymer pattern to promote and guide the growth of cells. Using the inkjet-printed Ppy/collagen scaffold, they were able to study the influence of the electrical stimulation and the outgrowth of neurite from the PC12 cells. Figure 12.14 shows the images of PC12 cells grown on the inkjet-printed Ppy/collagen scaffold.

12.4 Polythiophene (Pth) and Poly(3,4-Ethylenedioxythiophene) (PEDOT)

12.4.1 Properties and Synthesis of Pth and PEDOT Nanomaterials

Polythiophene (Pth), as shown in Figure 12.15a, is another well-known conjugated polymer formed by a chain of monomer repeat units, which has a form of a five-membered sulfur heterocycle. Its conductivity is highly responsive and sensitive to the exposure to various gas molecules [65]; hence, Pth is often utilized as a chemiresistive volatile organic compound (VOC) sensor. PEDOT, illustrated in Figure 12.15b, is also a highly conductive polymer with similar chemical structures. PEDOT is particularly interesting due to its optical transparency and high stability. PEDOT is commonly composited with polystyrene sulfonate (PSS) to form PEDOT:PSS, which enhances its solubility and therefore its solution processability.

12.4.2 Inkjet Printing and Applications of Pth Nanomaterials

Li *et al.* have implemented an inkjet-printed Pth-based VOC sensor array [66] where a 4×6 chemiresistive sensor array was developed with each sensor having a unique type of polythiophene derivatives such as poly(3-hexylthiophene) (P3HT) and poly(3-dodecylthiophene) (PDDT). Furthermore, they have used principal component analysis (PCA) to reduce the dimension of the sensor data into a few uncorrelated vector components. With this technique, they were able to distinguish various VOCs from one another including methanol, isopropanol, acetonitrile, toluene, and benzene to name a few. The inkjet-printed Pth-based sensor is shown in Figure 12.16, where the polymer was deposited on each spiral electrode to form a resistive junction. Chuang *et al.* have inkjet-printed PEDOT:PSS blended with SiO_2 nanoparticles to develop a resistive humidity sensor [67]. Inkjet printing has also been applied to the fabrication of polymer solar cells [68].

12.5 Conclusions and Future Outlook

Although inkjet-printing technique has been around for many years, it was not until in recent years that researchers have started applying this technology to the

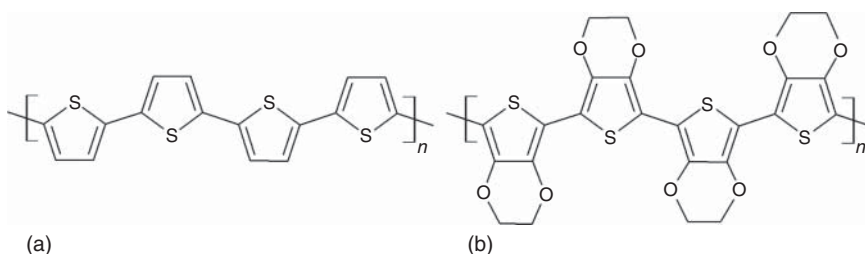


Figure 12.15 General chemical structures of (a) polythiophene and (b) poly(3,4-ethylenedioxythiophene) (PEDOT).

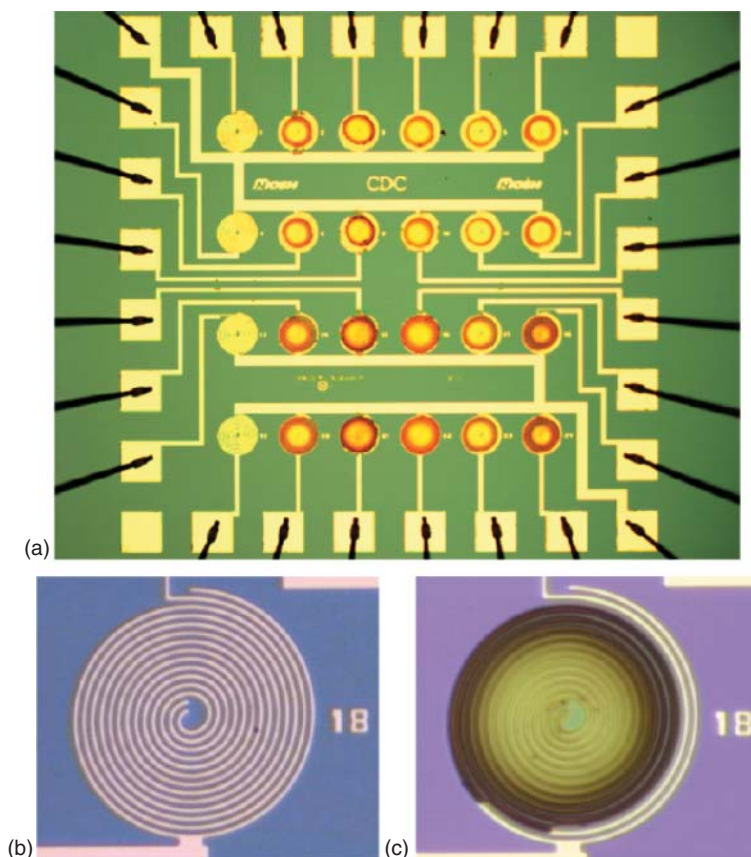


Figure 12.16 An inkjet-printed VOC sensor array. (a) Completed, wire bonded, test chip showing 24 electrode patterns with ink-jetted polymers. The sensors in the first column were used for reference. The rest of the electrodes have one type polymer (polythiophene derivative) jetted on each column. (b) Enlarged view of the gold spiral electrodes with no polymer. (c) Spiral electrodes with jetted poly(3-hexylthiophene) polymer formed from 10 drops of 5 mg ml^{-1} polymer concentration dissolved in trichlorobenzene. (Chuang *et al.* (2012) [67]. Reproduced with permission of IEEE.)

fabrication of printable and flexible electronic devices. Over the past decade or so, we have seen an explosion of publications on the inkjet printing of nanoformulations including nanoparticles, nanotubes, nanowires, and nanofibers. Conducting polymer nanomaterials continue to be a subject of great interest due to the numerous applications where they can be used. The authors believe that inkjet printing of conducting polymer nanomaterials will be at the forefront of printable electronics as well as flexible and wearable electronics. With this technology still in its infancy, there are several key issues and challenges that need to be addressed before the technology can be useful in practical industrial applications. Dispersion and suspension of the nanomaterials in liquid phase while keeping the viscosity and surface tension of the liquid under the printable condition still remain

a major challenge for inkjet printing of nanomaterials. For reliable printing operation and for avoiding the clogging of printer nozzles, no agglomeration of the nanomaterial should occur throughout the printing process. For multiple layer deposition, alignment of each print layer should also be better controlled especially for microscale feature sizes. Pattern resolution is another important issue. Commercially available inkjet printers are capable of achieving a minimum resolution of a few tens of microns. However, with enhanced patterning capability, the application of inkjet-printed nanomaterials could be expanded even further to areas requiring delicate and complex features such as transistor fabrication and nanoelectronics.

References

- 1 Singh, M., Haverinen, H.M., Dhagat, P., and Jabbour, G.E. (2010) Inkjet printing—process and its applications. *Adv. Mater.*, **22** (6), 673–685.
- 2 Tekin, E., Smith, P.J., and Schubert, U.S. (2008) Inkjet printing as a deposition and patterning tool for polymers and inorganic particles. *Soft Matter*, **4** (4), 703–713.
- 3 Zhu, C., Yang, G., Li, H., Du, D., and Lin, Y. (2015) Electrochemical sensors and biosensors based on nanomaterials and nanostructures. *Anal. Chem.*, **87** (1), 230–249.
- 4 Reddinger, J.L. and Reynolds, J.R. (1999) Molecular engineering of π -conjugated polymers, in *Radical Polymerisation Polyelectrolytes* (eds I. Capek, J. Hernández-Barajas, D. Hunkeler, J.L. Reddinger, J.R. Reynolds, and C. Wandrey), Springer, Berlin, Heidelberg, pp. 57–122.
- 5 MacDiarmid, A.G. and Epstein, A.J. (1989) Polyanilines: A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.*, **88**, 317–332.
- 6 Syed, A.A. and Dinesan, M.K. (1991) Review: Polyaniline—a novel polymeric material. *Talanta*, **38** (8), 815–837.
- 7 Geniès, E.M., Boyle, A., Lapkowski, M., and Tsintavis, C. (1990) Polyaniline: A historical survey. *Synth. Met.*, **36** (2), 139–182.
- 8 Huang, W.-S., Humphrey, B.D., and MacDiarmid, A.G. (1986) Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc. Faraday Trans. 1*, **82** (8), 2385–2400.
- 9 Tran, H.D., Wang, Y., D'Arcy, J.M., and Kaner, R.B. (2008) Toward an understanding of the formation of conducting polymer nanofibers. *ACS Nano*, **2** (9), 1841–1848.
- 10 Paul, E.W., Ricco, A.J., and Wrighton, M.S. (1985) Resistance of polyaniline films as a function of electrochemical potential and the fabrication of polyaniline-based microelectronic devices. *J. Phys. Chem.*, **89** (8), 1441–1447.
- 11 Focke, W.W., Wnek, G.E., and Wei, Y. (1987) Influence of oxidation state, pH, and counterion on the conductivity of polyaniline. *J. Phys. Chem.*, **91** (22), 5813–5818.
- 12 Song, E. and Choi, J.-W. (2013) Conducting polyaniline nanowire and its applications in chemiresistive sensing. *Nanomaterials*, **3** (3), 498–523.

- 13 Yue, J. and Epstein, A.J. (1990) Synthesis of self-doped conducting polyaniline. *J. Am. Chem. Soc.*, **112** (7), 2800–2801.
- 14 Li, C. and Mu, S. (2005) The electrochemical activity of sulfonic acid ring-substituted polyaniline in the wide pH range. *Synth. Met.*, **149** (2–3), 143–149.
- 15 Lukachova, L.V., Shkerin, E.A., Puganova, E.A., Karyakina, E.E., Kiseleva, S.G., Orlov, A.V., Karpacheva, G.P., and Karyakin, A.A. (2003) Electroactivity of chemically synthesized polyaniline in neutral and alkaline aqueous solutions: Role of self-doping and external doping. *J. Electroanal. Chem.*, **544**, 59–63.
- 16 Zhang, L. and Dong, S. (2004) The electrocatalytic oxidation of ascorbic acid on polyaniline film synthesized in the presence of camphorsulfonic acid. *J. Electroanal. Chem.*, **568**, 189–194.
- 17 Lee, K.-H., Park, B.J., Song, D.H., Chin, I.-J., and Choi, H.J. (2009) The role of acidic m-cresol in polyaniline doped by camphorsulfonic acid. *Polymer*, **50** (18), 4372–4377.
- 18 Del Castillo-Castro, T., Castillo-Ortega, M.M., Villarreal, I., Brown, F., Grijalva, H., Pérez-Tello, M., Nuño-Donlucas, S.M., and Puig, J.E. (2007) Synthesis and characterization of composites of DBSA-doped polyaniline and polystyrene-based ionomers. *Composites, Part A*, **38** (2), 639–645.
- 19 Haberkro, J., Bernasik, A., Łużny, W., Hasik, M., Raczkowska, J., Rysz, J., and Budkowski, A. (2013) Humidity and wetting effects in spin-cast blends of insulating polymers and conducting polyaniline doped with DBSA. *J. Appl. Polym. Sci.*, **127** (3), 2354–2361.
- 20 Raitman, O.A., Katz, E., Bückmann, A.F., and Willner, I. (2002) Integration of polyaniline/poly(acrylic acid) films and redox enzymes on electrode supports: An in situ electrochemical/surface plasmon resonance study of the bioelectrocatalyzed oxidation of glucose or lactate in the integrated bioelectrocatalytic systems. *J. Am. Chem. Soc.*, **124** (22), 6487–6496.
- 21 Tang, Y., Pan, K., Wang, X., Liu, C., and Luo, S. (2010) Electrochemical synthesis of polyaniline in surface-attached poly(acrylic acid) network, and its application to the electrocatalytic oxidation of ascorbic acid. *Microchim. Acta*, **168** (3–4), 231–237.
- 22 Bonastre, A.M., Sosna, M., and Bartlett, P.N. (2011) An analysis of the kinetics of oxidation of ascorbate at poly(aniline)-poly(styrene sulfonate) modified microelectrodes. *Phys. Chem. Chem. Phys.*, **13** (12), 5365–5372.
- 23 Bartlett, P.N. and Wang, J.H. (1996) Electroactivity, stability and application in an enzyme switch at pH 7 of poly(aniline)–poly(styrenesulfonate) composite films. *J. Chem. Soc., Faraday Trans.*, **92** (20), 4137–4143.
- 24 Stilwell, D.E. and Park, S.-M. (1988) Electrochemistry of conductive polymers II. Electrochemical studies on growth properties of polyaniline. *J. Electrochem. Soc.*, **135** (9), 2254–2262.
- 25 Kobayashi, T., Yoneyama, H., and Tamura, H. (1984) Electrochemical reactions concerned with electrochromism of polyaniline film-coated electrodes. *J. Electroanal. Chem. Interfacial Electrochem.*, **177** (1–2), 281–291.
- 26 Ofer, D., Crooks, R.M., and Wrighton, M.S. (1990) Potential dependence of the conductivity of highly oxidized polythiophenes, polypyrroles, and

- polyaniline: finite windows of high conductivity. *J. Am. Chem. Soc.*, **112** (22), 7869–7879.
- 27 Song, E. and Choi, J.-W. (2014) Self-calibration of a polyaniline nanowire-based chemiresistive pH sensor. *Microelectron. Eng.*, **116**, 26–32.
 - 28 Huang, J., Virji, S., Weiller, B.H., and Kaner, R.B. (2003) Polyaniline nanofibers: Facile synthesis and chemical sensors. *J. Am. Chem. Soc.*, **125** (2), 314–315.
 - 29 Zhang, X., Goux, W.J., and Manohar, S.K. (2004) Synthesis of polyaniline nanofibers by ‘nanofiber seeding.’ *J. Am. Chem. Soc.*, **126** (14), 4502–4503.
 - 30 Huang, J. and Kaner, R.B. (2004) A general chemical route to polyaniline nanofibers. *J. Am. Chem. Soc.*, **126** (3), 851–855.
 - 31 Huang, J. and Kaner, R.B. (2004) Nanofiber formation in the chemical polymerization of aniline: A mechanistic study. *Angew. Chem.*, **116** (43), 5941–5945.
 - 32 Qiang, J., Yu, Z., Wu, H., and Yun, D. (2008) Polyaniline nanofibers synthesized by rapid mixing polymerization. *Synth. Met.*, **158** (13), 544–547.
 - 33 Ngamna, O., Morrin, A., Killard, A.J., Moulton, S.E., Smyth, M.R., and Wallace, G.G. (2007) Inkjet printable polyaniline nanoformulations. *Langmuir*, **23** (16), 8569–8574.
 - 34 Jang, J., Ha, J., and Cho, J. (2007) Fabrication of water-dispersible polyaniline-poly(4-styrenesulfonate) nanoparticles for inkjet-printed chemical-sensor applications. *Adv. Mater.*, **19** (13), 1772–1775.
 - 35 Song, E., Tortorich, R.P., da Costa, T.H., and Choi, J.-W. (2015) Inkjet printing of conductive polymer nanowire network on flexible substrates and its application in chemical sensing. *Microelectron. Eng.*, **145**, 143–148.
 - 36 Calvert, P. (2001) Inkjet printing for materials and devices. *Chem. Mater.*, **13** (10), 3299–3305.
 - 37 Gomes, T.C., Constantino, C.J.L., Lopes, E.M., Job, A.E., and Alves, N. (2012) Thermal inkjet printing of polyaniline on paper. *Thin Solid Films*, **520** (24), 7200–7204.
 - 38 Setti, L., Fraleoni-Morgera, A., Ballarin, B., Filippini, A., Frascaro, D., and Piana, C. (2005) An amperometric glucose biosensor prototype fabricated by thermal inkjet printing. *Biosens. Bioelectron.*, **20** (10), 2019–2026.
 - 39 Wang, J., Chan, S., Carlson, R.R., Luo, Y., Ge, G., Ries, R.S., Heath, J.R., and Tseng, H.-R. (2004) Electrochemically fabricated polyaniline nanoframe-work electrode junctions that function as resistive sensors. *Nano Lett.*, **4** (9), 1693–1697.
 - 40 Crowley, K., O'Malley, E., Morrin, A., Smyth, M.R., and Killard, A.J. (2008) An aqueous ammonia sensor based on an inkjet-printed polyaniline nanoparticle-modified electrode. *Analyst*, **133** (3), 391–399.
 - 41 Carrasco, P.M., Grande, H.J., Cortazar, M., Alberdi, J.M., Areizaga, J., and Pomposo, J.A. (2006) Structure–conductivity relationships in chemical polypyrroles of low, medium and high conductivity. *Synth. Met.*, **156** (5–6), 420–425.
 - 42 Turco, A., Corvaglia, S., and Mazzotta, E. (2015) Electrochemical sensor for sulfadimethoxine based on molecularly imprinted polypyrrole: Study of imprinting parameters. *Biosens. Bioelectron.*, **63**, 240–247.

- 43 Hosono, K., Matsubara, I., Murayama, N., Woosuck, S., and Izu, N. (2005) Synthesis of polypyrrole/MoO₃ hybrid thin films and their volatile organic compound gas-sensing properties. *Chem. Mater.*, **17** (2), 349–354.
- 44 Mortimer, R.J., Dyer, A.L., and Reynolds, J.R. (2006) Electrochromic organic and polymeric materials for display applications. *Displays*, **27** (1), 2–18.
- 45 Diaz, A.F., Castillo, J.I., Logan, J.A., and Lee, W.-Y. (1981) Electrochemistry of conducting polypyrrole films. *J. Electroanal. Chem. Interfacial Electrochem.*, **129** (1), 115–132.
- 46 Yeu, T., Yin, K.-M., Carbajal, J., and White, R.E. (1991) Electrochemical characterization of electronically conductive polypyrrole on cyclic voltamograms. *J. Electrochem. Soc.*, **138** (10), 2869–2877.
- 47 Wu, C.-G. and Bein, T. (1994) Conducting carbon wires in ordered, nanometer-sized channels. *Science*, **266** (5187), 1013–1015.
- 48 Martin, C.R. (1994) Nanomaterials: A membrane-based synthetic approach. *Science*, **266** (5193), 1961–1966.
- 49 Duchet, J., Legras, R., and Demoustier-Champagne, S. (1998) Chemical synthesis of polypyrrole: Structure–properties relationship. *Synth. Met.*, **98** (2), 113–122.
- 50 Zhang, X., Zhang, J., Song, W., and Liu, Z. (2006) Controllable synthesis of conducting polypyrrole nanostructures. *J. Phys. Chem. B*, **110** (3), 1158–1165.
- 51 Ma, Y., Zhang, J., Zhang, G., and He, H. (2004) Polyaniline nanowires on Si surfaces fabricated with DNA templates. *J. Am. Chem. Soc.*, **126** (22), 7097–7101.
- 52 Fan, Y., Chen, X., Trigg, A.D., Tung, C., Kong, J., and Gao, Z. (2007) Detection of MicroRNAs using target-guided formation of conducting polymer nanowires in nanogaps. *J. Am. Chem. Soc.*, **129** (17), 5437–5443.
- 53 Goren, M. and Lennox, R.B. (2001) Nanoscale polypyrrole patterns using block copolymer surface micelles as templates. *Nano Lett.*, **1** (12), 735–738.
- 54 Hatano, T., Bae, A.-H., Takeuchi, M., Fujita, N., Kaneko, K., Ihara, H., Takafuji, M., and Shinkai, S. (2004) Helical superstructure of conductive polymers as created by electrochemical polymerization by using synthetic lipid assemblies as a template. *Angew. Chem.*, **116** (4), 471–475.
- 55 Weng, B., Shepherd, R., Chen, J., and Wallace, G.G. (2011) Gemini surfactant doped polypyrrole nanodispersions: An inkjet printable formulation. *J. Mater. Chem.*, **21** (6), 1918–1924.
- 56 Zhang, X., Zhang, J., Liu, Z., and Robinson, C. (2004) Inorganic/organic mesostructure directed synthesis of wire/ribbon-like polypyrrole nanostructures. *Chem. Commun.*, (16), 1852–1853.
- 57 Wu, A., Kolla, H., and Manohar, S.K. (2005) Chemical synthesis of highly conducting polypyrrole nanofiber film. *Macromolecules*, **38** (19), 7873–7875.
- 58 Blinova, N.V., Stejskal, J., Trchová, M., Prokeš, J., and Omastová, M. (2007) Polyaniline and polypyrrole: A comparative study of the preparation. *Eur. Polym. J.*, **43** (6), 2331–2341.
- 59 Zang, J., Li, C.M., Bao, S.-J., Cui, X., Bao, Q., and Sun, C.Q. (2008) Template-free electrochemical synthesis of superhydrophilic polypyrrole nanofiber network. *Macromolecules*, **41** (19), 7053–7057.

- 60 Zhang, X. and Manohar, S.K. (2005) Narrow pore-diameter polypyrrole nanotubes. *J. Am. Chem. Soc.*, **127** (41), 14156–14157.
- 61 Zhang, W., Yang, F.K., Pan, Z., Zhang, J., and Zhao, B. (2014) Bio-inspired dopamine functionalization of polypyrrole for improved adhesion and conductivity. *Macromol. Rapid Commun.*, **35** (3), 350–354.
- 62 Mabrook, M.F., Pearson, C., and Petty, M.C. (2006) Inkjet-printed polypyrrole thin films for vapour sensing. *Sens. Actuators, B*, **115** (1), 547–551.
- 63 Weng, B., Morrin, A., Shepherd, R., Crowley, K., Killard, A.J., Innis, P.C., and Wallace, G.G. (2014) Wholly printed polypyrrole nanoparticle-based biosensors on flexible substrate. *J. Mater. Chem. B*, **2** (7), 793–799.
- 64 Weng, B., Liu, X., Shepherd, R., and Wallace, G.G. (2012) Inkjet printed polypyrrole/collagen scaffold: A combination of spatial control and electrical stimulation of PC12 cells. *Synth. Met.*, **162** (15–16), 1375–1380.
- 65 Hanawa, T., Kuwabata, S., Hashimoto, H., and Yoneyama, H. (1989) Gas sensitivities of electropolymerized polythiophene films. *Synth. Met.*, **30** (2), 173–181.
- 66 Li, B., Santhanam, S., Schultz, L., Jeffries-EL, M., Iovu, M.C., Sauvé, G., Cooper, J., Zhang, R., Revelli, J.C., Kusne, A.G., Snyder, J.L., Kowalewski, T., Weiss, L.E., McCullough, R.D., Fedder, G.K., and Lambeth, D.N. (2007) Inkjet printed chemical sensor array based on polythiophene conductive polymers. *Sens. Actuators, B*, **123** (2), 651–660.
- 67 W.-Y. Chuang, C.-H. Lee, C.-T. Lin, S.-H. Lin, and W.-J. Wu, *An Inkjet-Printed Humidity Sensor based on SiO₂ Nano Particle Blended PEDOT:PSS Films*, in 2012 IEEE Sensors, 2012, pp. 1–4.
- 68 Eom, S.H., Park, H., Mujawar, S.H., Yoon, S.C., Kim, S.-S., Na, S.-I., Kang, S.-J., Khim, D., Kim, D.-Y., and Lee, S.-H. (2010) High efficiency polymer solar cells via sequential inkjet-printing of PEDOT:PSS and P3HT:PCBM inks with additives. *Org. Electron.*, **11** (9), 1516–1522.

13

Application of Printed Silver Nanowires Based on Laser-Induced Forward Transfer

Teppei Araki, Rajesh Mandamparambil, Jinting Jiu, Tsuyoshi Sekitani, and Katsuaki Suganuma

13.1 Introduction

Conductive wiring is designed to achieve high signal integrity on rigid printed circuit boards. The mechanical flexibility and stretchability of such wiring is being developed for wearable electronics, to allow for their bending, twisting, stretching, and compression from human interaction [1–19]. These devices are often constructed on soft polymer substrates or clothing to allow for deformation; hence wiring plays an important role among the flexible and stretchable parts. The wiring must withstand high strain to be sufficiently soft for use in wearable electronic devices. The ability of the active components to sustain even a few percent strain is important for minimizing device degradation (Figure 13.1).

Silver nanowires (Ag NWs) are good candidates for such applications. Their high conductivity favors their miniaturization and high-density integration, compared with carbon nanotubes (CNTs) [1, 2], graphenes [3, 4], conductive polymers [5, 6], and metal particles [7–10]. High-aspect-ratio Ag NWs [7, 8] of diameter of 30–200 nm and length of 10–200 μm can be used to form high percolation networks. These silver-stabilized networks can exhibit good optical transparency and high conductivity of $6.3 \times 10^5 \text{ S cm}^{-1}$. Hence, Ag NWs are attractive materials for flexible transparent electrodes that cannot be realized by conventional tin-doped indium oxide (ITO)-based transparent electrodes. The mass production of large-area wearable electronics will likely require devices to be fabricated by roll-to-roll or sheet-to-sheet processes. Ag NWs can be synthesized on a large scale by simple solution processes, so they are ideal for realizing wearable electronics.

This chapter introduces transparent and stretchable electrodes based on Ag NWs. Long Ag NWs can be synthesized by a modified polyol method to obtain low sheet resistance and high transparent electrodes [11]. The patterning of stretchable electrodes based on Ag NWs is also important. Methods for fabricating Ag NW electrodes include flexographic printing, offset printing, screen printing, inkjet printing, imprinting, slot die coating, and laser-induced forward transfer (LIFT) [12]. LIFT is a promising technique for additive patterning under noncontact mode.

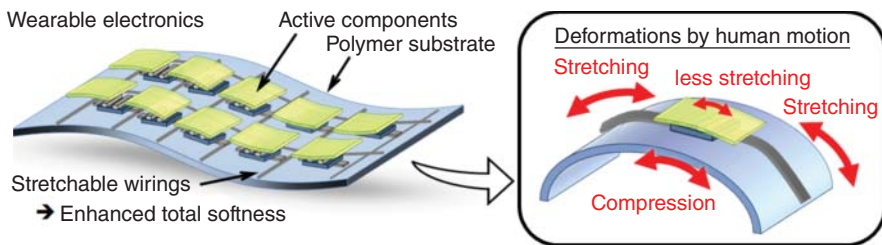


Figure 13.1 The softness of wearable devices is enhanced using stretchable wiring.

13.2 Ag NW Transparent Electrodes

13.2.1 Background

Ag NW transparent electrodes were first reported by Lee *et al.* of Stanford University in 2008. The performance of Ag NW transparent electrodes (optical transmittance: 86%, sheet resistance: $16 \Omega \square^{-1}$) was shown to be comparable to that of ITO transparent electrodes, and they exhibited high durability when subjected to bending [13]. The Ag NW transparent electrodes were compatible with bar coating [14] and spray coating [15] of solution techniques. This potentially allows Ag NW networks to be printed as transparent electrodes using roll-to-roll processes. Ag NW transparent electrodes have subsequently been investigated for flexible applications in organic solar cells, organic light-emitting devices, and tough panels [13, 15–19].

The application of transparent electrodes in displays requires low sheet resistance and high transparency with low haze. Haze is the ratio of the diffusivity to total transmittance. Table 13.1 shows the properties of transparent electrodes fabricated by ITO, CNTs, graphene, and Ag NWs. ITO electrodes exhibit a sheet resistance of $50 \Omega \square^{-1}$ and haze of 1–3% at 85% optical transmittance [14, 20, 21]. Fabricating ITO requires temperatures $>300^\circ\text{C}$, which is not recommended for polymer substrates (polycarbonate, polyethylene terephthalate, polyurethane, etc.) because of their low glass transition temperatures (T_g) of $\sim 100^\circ\text{C}$. Fabricating ITO also involves vacuum conditions, which is time consuming and costly. CNTs, graphene, and Ag NWs can all be deposited by simple wet processes, at below the T_g of the polymer substrate. CNTs and graphene transparent electrodes exhibit sheet resistances of over $>100 \Omega \square^{-1}$

Table 13.1 Performance of transparent electrodes fabricated from various materials.

	Typical Ag NWs	CNT and graphene	ITO	Ultra-long Ag NWs
Optical transmittance	90%	90%	85%	94–97%
Sheet resistance	$20\text{--}100 \Omega \square^{-1}$	$>100 \Omega \square^{-1}$	$50 \Omega \square^{-1}$	$24\text{--}109 \Omega \square^{-1}$
Haze	5–15%	$<1\%$	1–3%	1.6–3.4%

at a haze of <1% and 90% optical transmittance [22–26]. Graphene monolayer transparent electrodes exhibit the highest optical transmittance of 97%, with a sheet resistance of $>125 \Omega \square^{-1}$ [27]. Ag NW transparent electrodes exhibit the lowest sheet resistance of $20\text{--}100 \Omega \square^{-1}$ at 90% optical transmittance [14, 21, 25, 28–30]. However, Ag NWs of length of $\sim 20 \mu\text{m}$ and diameter of $\sim 70 \text{ nm}$ can result in a haze of 5–15%, which is disadvantageous in display applications. The high haze largely arises from the Ag NWs scattering incident light.

13.2.2 Transparent Electrodes Formed from Ultra-Long Ag NWs

Kim *et al.* of the Korea Advance Institute of Science and Technology showed that haze and optical transmittance are inversely proportional in Ag NW transparent electrodes [21]. Thus, low haze can be obtained by increasing the optical transmittance. An equivalent haze of <3% (3% is the haze of ITO-based transparent electrodes) was achieved for Ag NW transparent electrodes at >95% optical transmittance. In practice, Ag NW networks may not electrically conduct at such high optical transmittance. High-aspect-ratio Ag NW networks can be exploited to achieve low haze while maintaining the conductive network. These can be formed by increasing the Ag NW length or decreasing the Ag NW diameter. We synthesized ultra-long Ag NWs by a modified polyol method, and the resulting transparent electrode exhibited improved haze and optical transmittance (Table 13.1) [11].

Ag NWs were synthesized by reducing silver nitrate in ethylene glycol containing polyvinylpyrrolidone (PVP). After reaction, the solution was centrifuged with ethanol, and the product was dispersed in ethanol for further use. Typical Ag NWs were synthesized at 150°C for 1 h. The final Ag NWs had an average length of $11 \mu\text{m}$ and diameter of 68 nm (Figure 13.2a). Higher temperatures led to a higher rate of reduction [31], which limited the amount of Ag^+ source contributing to Ag NW growth. Hence, the Ag NWs tended to remain shorter at higher temperatures. Ultra-long Ag NWs were synthesized by decreasing the reaction temperature to 110°C and by decreasing the stirring speed so as to not disturb the Ag NWs grown at high Ag^+ concentration. The Ag NWs had an average length of $44 \mu\text{m}$ (maximum length: $230 \mu\text{m}$) and an average diameter of 91 nm

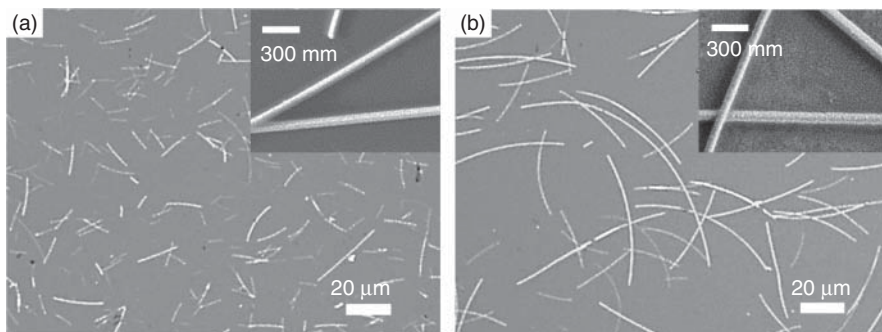


Figure 13.2 Optical microscopy images of (a) typical and (b) ultra-long Ag NWs. Insets show scanning electron microscopy (SEM) images.

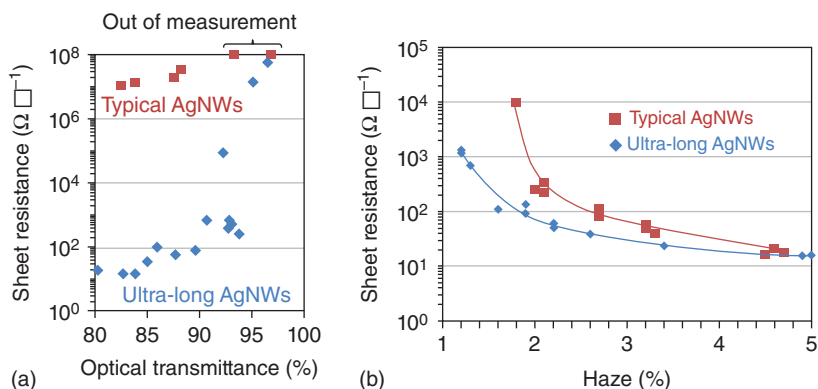


Figure 13.3 (a) Sheet resistance corresponding to optical transmittance for air-dried transparent electrodes. (b) Relationship between sheet resistance and haze for heated transparent electrodes at 200 °C for 10 min.

(Figure 13.2b). The high-aspect-ratio (484) and ultra-long Ag NWs were realized by the low reaction temperature and stirring speed. Their length was almost thrice that of typical Ag NWs.

Figure 13.3a shows the sheet resistance of an electrode prepared by drop-coating an ethanol suspension of Ag NWs onto a glass substrate, followed by drying in air. The transparent electrode containing ultra-long Ag NWs had a sheet resistance of $19\text{--}680 \Omega \square^{-1}$ and an optical transmittance of 80–91%. Typical electrodes fabricated at room temperature were not conductive. This difference reflected the differing morphologies of the networks and the contact between the Ag NWs. Contact resistances between wires are generally high because the dielectric PVP acts as a capping agent during synthesis [14]. Fewer contact points lower the contact resistance of the overall network. The ultra-long Ag NWs contained 1×10^{10} wires m^{-2} at an optical transmittance of 95%, which was seven times fewer wires than the transparent electrode containing typical Ag NWs. Fewer wires in the ultra-long Ag NW transparent electrode yielded a lower sheet resistance, because of the lower contact resistance. The larger diameter of the ultra-long Ag NWs increased the contact area between the wires, which also lowered the contact resistance of the transparent electrode. At room temperature fabrication, the sheet resistance was significantly affected by the Ag NW morphology. The higher aspect ratio and larger diameter ultra-long Ag NWs yielded a more conductive network.

The sheet resistance can be reduced by removing the PVP capping agent or by reducing the interwire gap by heating, high-intensity pulsed irradiation, or mechanical pressing [14, 17, 32]. Figure 13.3b shows the sheet resistance and haze of Ag NW transparent electrodes heated at 200 °C for 10 min. Heating led to decreased sheet resistances for electrodes of >90% optical transmittance. A transparent electrode consisting of ultra-long Ag NWs exhibited a sheet resistance of $24\text{--}109 \Omega \square^{-1}$ and haze of 3.4–1.6% at optical transmittance of 94–97%, compared to a typical Ag NW network transparent electrode, which exhibited a resistance of $>112 \Omega \square^{-1}$. This indicated higher performance of the

ultra-long Ag NWs, compared with ITO. The performance of the ultra-long Ag NW electrode was comparable to that of a monolayer graphene sheet, with a sheet resistance of $125 \Omega \square^{-1}$ at 97% optical transmittance [27].

13.3 Printed Ag NW Electrodes

13.3.1 Fabrication and Properties of Stretchable Electrodes

Ultra-long Ag NWs with high aspect ratios have been developed to retain their network structure upon stretching. Stretchable electrodes have been developed by mechanical transfer and coating methods. Hu *et al.* prepared a transparent conductive electrode by spraying an Ag NW dispersion onto a transparent substrate and then coating the deposited layer with a polyacrylic acid-based resin [33]. The resulting composite exhibited a sheet resistance of $7.5 \Omega \square^{-1}$ at 80% optical transmittance and could be stretched by up to 50% strain. Stretchable electrodes have also been fabricated by transferring Ag NW films onto rubber substrates. Xu *et al.* prepared stretchable Ag NW/polydimethylsiloxane (PDMS) electrodes [34]. Ag NW tracks were fabricated on the outermost surface of PDMS by transferring process. The stretchable electrode exhibited an initial resistivity of $1 \times 10^{-4} \Omega \text{ cm}$. The electrode exhibited a wrinkled structure after an initial stretching cycle of $\sim 100\%$ strain and stable electrical behavior after subsequent stretching at 60% strain. Lee *et al.* transferred an Ag NW film after Ag NWs solution was filtered. The Ag NW network remained on a membrane filter and then was transferred on an Ecoflex substrate [7]. Prestretching the substrate during transfer allowed the electrode to be stretched over five times its initial length. The aforementioned processes for depositing Ag NW electrodes are limited to the type of coating method. The patterned deposition of Ag NWs has received little attention, despite its excellent compatibility with solution processes.

13.3.2 Ag NWs Printing by LIFT

Developing patterning techniques for Ag NWs is important for next-generation wearable electronics. Maskless additive patterning is an attractive approach because of its design freedom and low material usage. Noncontact processes are also essential to avoid damaging prepatterned components already placed on the transfer area. Inkjet printing is one potential technique, but Ag NWs tend to clog inkjet nozzles, giving reliability problems. In this chapter, the patterning of Ag NWs by noncontact LIFT (Figure 13.4) is discussed [35–37].

LIFT is a promising technique for realizing digital manufacturing by non-contact stacking and maskless patterning. LIFT involves a target material on a donor substrate being injected toward an acceptor substrate by laser illumination (Figure 13.4a). The donor consists of a transparent substrate, dynamic release layer (DRL), and target layer. The laser radiation is incident on the DRL through the transparent substrate and causes the DRL to be ablated and become vaporized. The volume difference from solid to vapor propels the target material toward the acceptor substrate. Recently, Ag NW deposition by inkjet printing

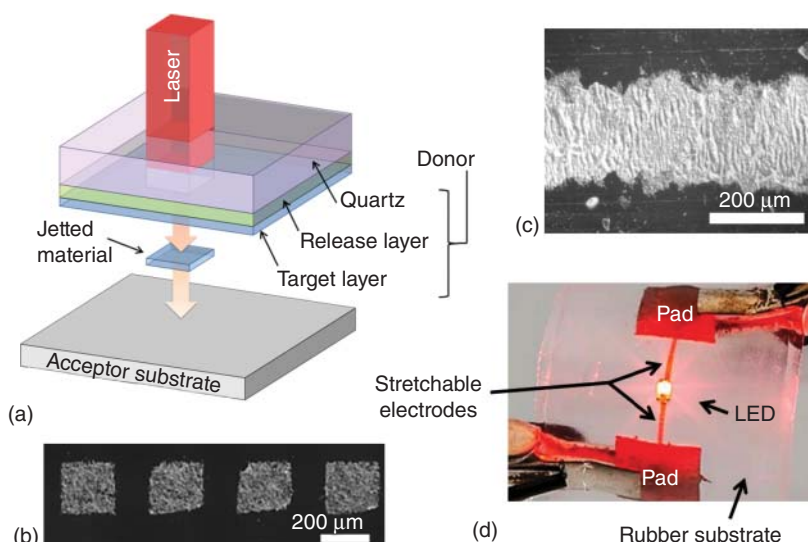


Figure 13.4 Noncontact printing by LIFT. (a) Schematic of the LIFT process. (b) Printed Ag NW network bound with resin, observed by optical microscopy. (c) Optical microscopy images of printed a stretchable Ag NW track prepared by prestretching. (d) Illuminated LED connected by stretchable track on a rubber substrate.

was reported with optimizations of ink viscosity and particle size [38, 39]. However, LIFT is a versatile technique for noncontact printing because various viscosity materials from solids to liquids can be used as the target layer.

To prepare the donor, an ultra-long Ag NW film was fabricated on a quartz substrate with a DRL, by drop casting Ag NW solution and subsequent deposition of a binder. The Ag NW film was illuminated from the quartz side by a laser energy fluence of $\sim 70 \text{ mJ cm}^{-2}$ and with a square beam shape of size $\sim 5 \times 10^4 \mu\text{m}^2$. This caused a small area of the Ag NW film to be pushed toward and transferred onto the acceptor substrate (Figure 13.4b). The source was a nanosecond laser with a wavelength of 248 nm.

Conductive tracks were fabricated by stitching together transferred films, and the electrical resistivity of the resulting tracks was $1 \times 10^{-4} \Omega \text{ cm}$. Tracks were typically several millimeter long and $\sim 200 \mu\text{m}$ wide. Tracks fabricated by prestretching (Figure 13.4c) exhibited excellent stretchability at 100% strain, while retaining a resistance increase of less than twice the initial resistance. Wrinkles formed by prestretching the Ag NW track enhanced the stretchability. Stretching experiments confirmed that the electrical resistances of transferred tracks were stable over 10 cycles, when stretched to 50% strain. A light-emitting diode (LED) integrated on the stretchable Ag NW track became illuminated after deformation (Figure 13.4d). Thus, noncontact additive manufacturing by LIFT is promising for patterning stretchable Ag NW tracks integrated in flexible and wearable electronics without mechanical damages.

13.4 Summary

Transparent stretchable electrodes of high-aspect-ratio Ag NWs can exhibit high mechanical flexibility and high conductivity. The haze of Ag NW transparent electrodes can be improved by increasing the Ag NW length to four times that of typical Ag NWs, using a modified polyol method. Transparent electrodes containing ultra-long Ag NWs exhibited high transparency and conductivity, even when fabricated at room temperature. A noncontact patterning process for depositing Ag NWs was developed based on LIFT, which yielded 100% stretchable tracks for wearable electronics. This process involving ultra-long Ag NWs was carried out as noncontact patterning and is therefore compatible with additive printing for design freedom and low materials usage. This makes it conducive to roll-to-roll printing and suggests its potential in preparing wearable devices.

References

- 1 Sekitani, T., Nakajima, H., Maeda, H. *et al.* (2009) Stretchable active-matrix organic light-emitting diode display using printable elastic conductors. *Nat. Mater.*, **8** (6), 494–499.
- 2 Lipomi, D.J., Vosgueritchian, M., Tee, B.C.-K. *et al.* (2011) Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes. *Nat. Nanotechnol.*, **6** (12), 788–792.
- 3 Kim, K.S., Zhao, Y., Jang, H. *et al.* (2009) Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, **457** (7230), 706–710.
- 4 Chen, T., Xue, Y., Roy, A.K., and Dai, L. (2014) Transparent and stretchable high-performance supercapacitors based on wrinkled graphene electrodes. *ACS Nano*, **8** (1), 1039–1046.
- 5 Lipomi, D.J., Lee, J.a., Vosgueritchian, M. *et al.* (2012) Electronic properties of transparent conductive films of PEDOT:PSS on stretchable substrates. *Chem. Mater.*, **24** (2), 373–382.
- 6 Zheng, W., Razal, J.M., Whitten, P.G. *et al.* (2011) Artificial muscles based on polypyrrole/carbon nanotube laminates. *Adv. Mater.*, **23** (26), 2966–2970.
- 7 Lee, P., Lee, J., Lee, H. *et al.* (2012) Highly stretchable and highly conductive metal electrode by very long metal nanowire percolation network. *Adv. Mater.*, **24** (25), 3326–3332.
- 8 Ho, X., Nie Tey, J., Liu, W. *et al.* (2013) Biaxially stretchable silver nanowire transparent conductors. *J. Appl. Phys.*, **113** (4), 044311.
- 9 Ahn, B.Y., Duoss, E.B., Motala, M.J. *et al.* (2009) Omnidirectional printing of flexible, stretchable, and spanning silver microelectrodes. *Science*, **323** (5921), 1590–1593.
- 10 Araki, T., Nogi, M., Suganuma, K. *et al.* (2011) Printable and stretchable conductive wirings comprising silver flakes and elastomers. *IEEE Electron Device Lett.*, **32** (10), 1424–1426.

- 11 Araki, T., Jiu, J., Nogi, M. *et al.* (2014) Low haze transparent electrodes and highly conducting air dried films with ultra-long silver nanowires synthesized by one-step polyol method. *Nano Res.*, **7** (2), 236–245.
- 12 Araki, T., Mandamparambil, R., van Bragt, D. M. P. *et al.* (2016) Stretchable and transparent electrodes based on patterned silver nanowires by laser-induced forward transfer for non-contacted printing techniques. *Nanotechnology*, **2** (45), 45LT02.
- 13 Lee, J.-Y., Connor, S.T., Cui, Y., and Peumans, P. (2008) Solution-processed metal nanowire mesh transparent electrodes. *Nano Lett.*, **8** (2), 689–692.
- 14 Hu, L., Kim, H.S., Lee, J.-Y. *et al.* (2010) Scalable coating and properties of transparent, flexible, silver nanowire electrodes. *ACS Nano*, **4** (5), 2955–2963.
- 15 Madaria, A.R., Kumar, A., and Zhou, C. (2011) Large scale, highly conductive and patterned transparent films of silver nanowires on arbitrary substrates and their application in touch screens. *Nanotechnology*, **22** (24), 245201.
- 16 Gaynor, W., Lee, J.Y., and Peumans, P. (2010) Fully solution-processed inverted polymer solar cells with laminated nanowire electrodes. *ACS Nano*, **4** (1), 30–34.
- 17 Tokuno, T., Nogi, M., Karakawa, M. *et al.* (2011) Fabrication of silver nanowire transparent electrodes at room temperature. *Nano Res.*, **4** (12), 1215–1222.
- 18 Zeng, X.Y., Zhang, Q.K., Yu, R.M., and Lu, C.Z. (2010) A new transparent conductor: Silver nanowire film buried at the surface of a transparent polymer. *Adv. Mater.*, **22** (40), 4484–4488.
- 19 Yu, Z., Zhang, Q., Li, L. *et al.* (2011) Highly flexible silver nanowire electrodes for shape-memory polymer light-emitting diodes. *Adv. Mater.*, **23** (5), 664–668.
- 20 Gaskell, J.M. and Sheel, D.W. (2012) Deposition of indium tin oxide by atmospheric pressure chemical vapour deposition. *Thin Solid Films*, **520** (12), 4110–4113.
- 21 Kim, T., Canlier, A., Kim, G.H. *et al.* (2013) Electrostatic spray deposition of highly transparent silver nanowire electrode on flexible substrate. *ACS Appl. Mater. Interfaces*, **5** (3), 788–794.
- 22 Hecht, D.S., Ladous, C., Drzaic, P., and Fellow, S.I.D. (2009) Carbon-nanotube film on plastic as transparent electrode for resistive touch screens. *J. Soc. Inf. Disp.*, **17** (11), 941–946.
- 23 Yamada, T., Ishihara, M., and Hasegawa, M. (2013) Large area coating of graphene at low temperature using a roll-to-roll microwave plasma chemical vapor deposition. *Thin Solid Films*, **532**, 89–93.
- 24 Dan, B., Irvin, G.C., and Pasquali, M. (2009) Continuous and scalable fabrication of transparent conducting carbon nanotube films. *ACS Nano*, **3** (4), 835–843.
- 25 Hu, L., Wu, H., and Cui, Y. (2011) Metal nanogrids, nanowires, and nanofibers for transparent electrodes. *MRS Bull.*, **36** (10), 760–765.
- 26 Wu, J., Agrawal, M., Becerril, H.A. *et al.* (2009) Organic light-emitting diodes on solution-processed graphene transparent electrodes. *ACS Nano*, **4** (1), 43–48.
- 27 Bae, S., Kim, H., Lee, Y. *et al.* (2010) Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.*, **5** (8), 574–578.

- 28 De, S., Higgins, T.M., Lyons, P.E. *et al.* (2009) Silver nanowire networks as flexible, transparent, conducting films: Extremely high DC to optical conductivity ratios. *ACS Nano*, **3** (7), 1767–1774.
- 29 Katagiri, K. and Hunakubo, T. (2012) Metal nanowires, method for producing same, transparent conductor and touch panel, US 2012/0255762 A1.
- 30 Preston, C., Xu, Y., Han, X. *et al.* (2013) Optical haze of transparent and conductive silver nanowire films. *Nano Res.*, **6** (7), 461–468.
- 31 Bergin, S.M., Chen, Y.-H., Rathmell, A.R. *et al.* (2012) The effect of nanowire length and diameter on the properties of transparent, conducting nanowire films. *Nanoscale*, **4** (6), 1996–2004.
- 32 Garnett, E.C., Cai, W., Cha, J.J. *et al.* (2012) Self-limited plasmonic welding of silver nanowire junctions. *Nat. Mater.*, **11** (3), 241–249.
- 33 Hu, W., Niu, X., Li, L. *et al.* (2012) Intrinsically stretchable transparent electrodes based on silver-nanowire–crosslinked-polyacrylate composites. *Nanotechnology*, **23** (34), 344002.
- 34 Xu, F. and Zhu, Y. (2012) Highly conductive and stretchable silver nanowire conductors. *Adv. Mater.*, **24** (37), 5117–5122.
- 35 Bohandy, J., Kim, B.F., and Adrian, F.J. (1986) Metal deposition from a supported metal film using an excimer laser. *J. Appl. Phys.*, **60** (4), 1538–1539.
- 36 Perinchery, S.M., Smits, E.C.P., Sridhar, A. *et al.* (2014) Investigation of the effects of LIFT printing with a KrF-excimer laser on thermally sensitive electrically conductive adhesives. *Laser Phys.*, **24** (6), 066101.
- 37 Tseng, M.L., Wu, P.C., Sun, S. *et al.* (2012) Fabrication of multilayer meta-materials by femtosecond laser-induced forward-transfer technique. *Laser Photonics Rev.*, **6** (5), 702–707.
- 38 Lu, H., Lin, J., Wu, N. *et al.* (2015) Inkjet printed silver nanowire network as top electrode for semi-transparent organic photovoltaic devices. *Appl. Phys. Lett.*, **106** (9), 1–5.
- 39 Wang, P.-H., Chen, S.-P., Su, C.-H., and Liao, Y.-C. (2015) Direct printed silver nanowire thin film patterns for flexible transparent heaters with temperature gradient. *RSC Adv.*, **5**, 98412–98418.

14

Inkjet Printing of Functional Polymers into Carbon Fiber Composites

Patrick J. Smith, Elliot J. Fleet, and Yi Zhang

This chapter discusses the use of inkjet printing to deposit droplets of functional polymers into carbon fiber composites. The polymers enhance one or more mechanical properties, and inkjet printing is thought to confer additional benefits as each droplet is discrete, that is, each deposited droplet does not contact neighboring droplets to form films. The interest in carbon fiber composites as structural components is first discussed before highlighting concerns that ideally manufacturers and end-users would like to see addressed. The two main mechanical tests that are performed to assess composite properties are then discussed. These two tests provide the data that illustrate the advantage of including the inkjet-printed polymer droplets. The final section of the chapter discusses the printing of a synthesized monomer that delivers an intrinsic repair property to the composite system; heating initiates the repair.

14.1 Inkjet Printing

Inkjet printing is, as the reader of this book should now be aware of, a precise material deposition technique that finds its greatest application area in the realm of graphical printing. While graphical applications continue to be of great importance, inkjet is increasingly being considered and employed in a variety of technical fields such as printed electronics [1], conductors [2], RFID tags [3], and tissue engineering [4]. Printable materials can be biological, organic, or inorganic, forming inks that are either solutions or suspensions. The main advantage of inkjet involves the precise positioning of small, equally precise amounts of material on a substrate. Both the amount of material and the location are determined before the manufacture step is carried out. Inkjet appeals as structures can be made with minimal waste. Moreover, because inkjet is a direct write technology, the overall number of process steps taken is smaller compared to technologies such as photolithography or screen printing. Finally, another advantage is that additional printheads can be added to a system, making scale-up to mass production relatively simple.

14.2 Carbon Fiber Composites

The term composite material is used to describe a class of materials that consist of two or more discrete materials combined together in order to produce a synergistic effect. Typically, reinforcement is provided by one component and a second matrix component acts as a binder to protect the reinforcement and distribute the loads. The type of composite material that is most widely employed due to its high strength-to-weight ratio uses carbon fibers as the reinforcing material and epoxy resin as the matrix. The fibers are usually woven into a mat that is then impregnated with an epoxy resin, forming a sheet of material called pre-preg. The thermosetting resin in the pre-preg is typically then partially reacted, known as β -staging, in order to reduce resin bleed. Sheets of pre-preg are then laminated together in a process called “laying-up” before curing, typically using heat and pressure, to form the final structure. The process is the same for a class of composites called unidirectional, except the fibers are not woven – they are aligned in the same direction. Unidirectional pre-preg was the system used in the work discussed in this chapter.

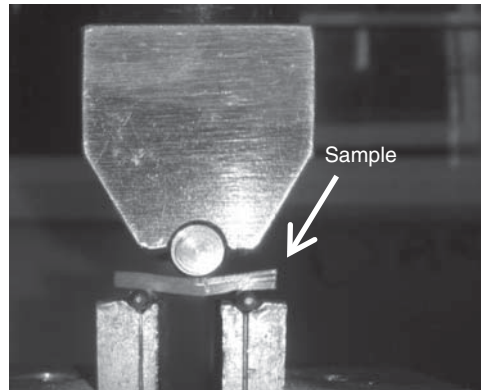
Due to their high specific stiffness and strength, carbon fiber composites are being increasingly used in aerospace applications, with specific examples being Airbus’s A350 XWB, which uses 52% of carbon fiber reinforced composites in its construction compared to Boeing’s 787 Dreamliner, which uses 50%. The driver for adopting carbon fiber composites is their weight, which directly contributes to fuel saving and, thereby, reduces greenhouse gas emissions. It has been calculated that for every kilogram removed from an aircraft’s weight an annual saving of 200 litres of fuel is made [5].

However, the recent adoption of carbon fiber composite materials in the primary structures of aircraft, such as the Dreamliner and the A350, has highlighted concerns over their low fracture toughness and brittleness. Carbon fiber composites do not visibly exhibit cracks or signs of fatigue in their early stages, which can result in time-consuming maintenance to ensure structural integrity. A common source of failure for carbon fiber composites is delamination, in which a crack forms and grows between the interface of the adjacent plies [6, 7]. A considerable amount of research has been directed toward addressing delamination, with approaches involving the addition of interfacial reinforcements [8–10] or the inclusion of self-healing systems [11, 12] or thermoplastic toughening agents [13, 14] into the bulk matrix. While these approaches are successful in increasing the toughness of the carbon fiber composites, other properties such as specific strength and modulus have decreased [15]. Weight has also been seen to increase.

14.3 Mechanical Tests

There are a number of standard tests that are performed to assess the mechanical properties of carbon fiber composites. Two of these tests are of interest to this chapter’s subject matter. The first test is known as short beam shear (SBS), which is commonly used to determine the apparent interlaminar shear strength (aILSS)

Figure 14.1 Short beam shear (SBS) test setup, showing a loaded sample of carbon fiber composite.



of the composite samples. The interlaminar shear strength is a measure of the maximum amount of shear stress a laminated material can tolerate between layers before failure. The principle of the test involves a three-point bend specimen configuration with a low support span to specimen thickness ratio; this configuration is chosen with an aim to create a shear failure between the plies of the material. It is not generally used to obtain design values, but for comparative purposes it is an extremely useful test. The standard SBS test used in this chapter prefers samples that are of 10 ± 0.2 mm wide and 2 ± 0.2 mm thick [16]. Eight layers of pre-preg were required for the samples discussed in this chapter, and each surface of the pre-preg had polymer droplets printed on them, which meant that a region of printed material was present in each interfacial region. The test apparatus is shown in Figure 14.1. A sample is mounted on two rollers and a third roller applies the load from above, pushing downward. The degree of loading can be controlled, which means the test can be halted before critical failure, which is useful for testing the efficiency of healing/repair experiments.

The second test measures the mode I critical strain energy release rate (G_{Ic}) and uses the double cantilever beam test apparatus [17]. The test, which will sometimes be called the DCB test in this chapter, measures how much energy is dissipated by the creation of new fracture surfaces upon initiation or propagation of cracks during delamination. This is a measure of how much strain energy is required to propagate a crack and can be used as an indicator of interlaminar fracture toughness. Samples for testing had the following dimensions: 140 ± 1 mm length, 20 ± 0.5 mm width, and 3 ± 0.1 mm thickness. A typical sample configuration is shown in Figure 14.2. A polytetrafluoroethylene (PTFE) film is inserted inside the sample at the midpoint of its thickness; the insert is used to allow the introduction of a crack. Only the midplane interface surface (the position of the PTFE insert) needs to be printed upon in the DCB test.

14.4 Printing and Sample Preparation

All of the printing that was used for the research discussed here was performed using the JetLab 4xl printer, which is a piezoelectric drop-on-demand printing

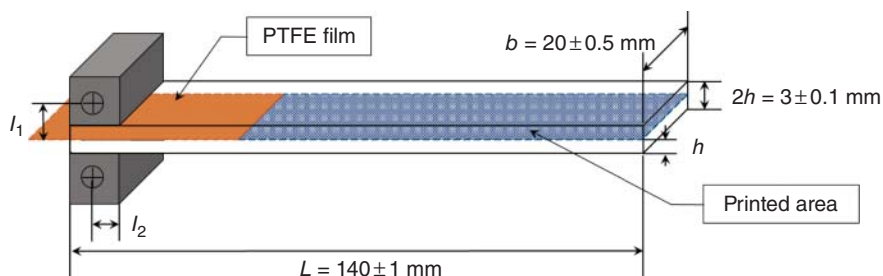


Figure 14.2 A schematic showing the test sample setup for the DCB test, a PTFE film is inserted to initiate cracking.

system supplied by MicroFab Inc. (Plano, USA). The JetLab 4xl is ideal for research purposes as it combines a high-quality waveform generation software package with piezoelectric glass nozzle printheads, which allows a researcher to use a wide range of experimental inks, solutions, and suspensions. The drawback of the system is that the printheads that are normally used are single nozzle, which means production rates are low (the SBS test specimens typically took 2 days to print). Although this is not a problem for fundamental research, it means scale-up research has to be transferred to another print system. The usual nozzle diameter used in the printing was 60 μm .

The two main inks were solutions that were composed of PMMA (poly(methyl methacrylate)) with a molecular weight of 15 000 Da dissolved in DMF (*N,N*-dimethylformamide), or of PEG (polyethylene glycol) dissolved in deionized water. The molecular weight of the PEG was 20 000 Da. All chemicals were purchased from Sigma Aldrich (Poole, UK). A third ink was prepared for the self-healing work, which is discussed in the relevant section. The concentration of the ink for both polymers ranged from 5% to 10% to 20%, with 10% being the preferred amount.

The substrate that was used in all of the reported research was a unidirectional carbon fiber reinforced polymer, CYCOM®977-2 that was supplied by Cytec Industries (Östringen, Germany). A customized autoclave (Premier Autoclaves Ltd., UK) was used to consolidate the laid-up panels. The curing cycle used for all composite samples followed the manufacturer's guidelines specified in the material data sheet and were as follows:

Temperature cycle: Heat from 20 °C to 180 °C at a rate of 1 °C min⁻¹, hold at 180 °C for 195 min, then cool back to 20 °C at 1 °C min⁻¹.

Pressure cycle: Increase pressure from 0 psi to 90 psi at a rate of 5 psi min⁻¹. Hold at 90 psi for 520 min and then decrease pressure back to 0 psi at a rate of 5 psi min⁻¹.

14.5 Carbon Fiber Composites that Contain Inkjet-Printed Patterns Composed of PMMA Microdroplets

As inkjet printing is a technique that can print a vast variety of patterns, the first effect that was examined was the influence that a printed pattern can have on

the G_{Ic} of the final composite. Four different discrete dot and line patterns were printed, alongside a continuous film. The concentration of the PMMA in DMF solution was set at 10 wt%. The four print patterns were designed to have the same amount of deposited PMMA per unit area. The four patterns are shown in Figure 14.3, along with their dot-spacing in X and Y [18].

After printing, lay-up, and curing, the four printed patterns were tested using DCB against a nonprinted control. The results are shown in Figure 14.4. All four of the printed patterns had improved interlaminar fracture toughness (denoted here as $G_{Ic(\text{initiation})}$, which is the value at the point the crack begins and $G_{Ic(\text{propagation})}$, the average value of interlaminar fracture as the crack propagates into the composite). The highest increase was for pattern 4, which was 40% compared to the nonprinted (NP) control. These results show that adding PMMA toughens the composite material and that the pattern employed has also an effect. All four patterns deposited the same amount of PMMA per unit area, but varied in terms of surface coverage. The value of surface coverage was calculated by dividing the area covered by printed PMMA deposits by the unit area. This calculation gave values of 24% surface coverage for patterns 1 and 2, which is due to droplet overlap, while patterns 3 and 4 covered about 37% of the surface.

A continuous film was also printed in which deposited droplets of PMMA overlapped each other in both X and Y . The DCB test results are shown in Figure 14.5. The reason for printing the continuous film was twofold. In the first instance, a film maximizes the amount of surface coverage; second, it mimics

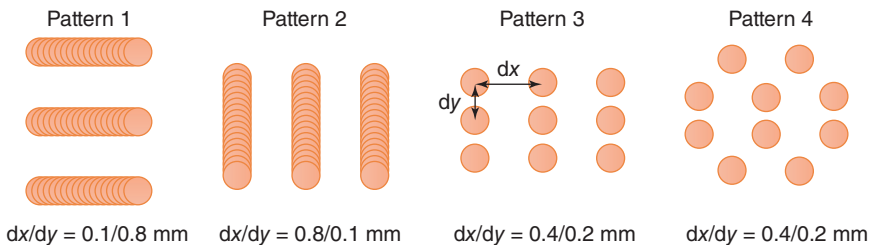


Figure 14.3 Four different print patterns that deposited an equal amount of PMMA per unit area of substrate. (Zhang *et al.* (2015) [18]. Reproduced with permission.)

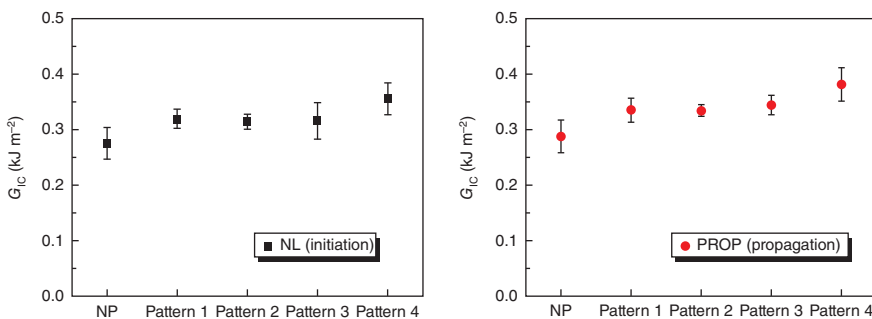


Figure 14.4 G_{Ic} comparison between NP and samples with printed different patterns (error bars represent standard deviation, $n = 5$). (Zhang *et al.* (2015) [18]. Reproduced with permission.)

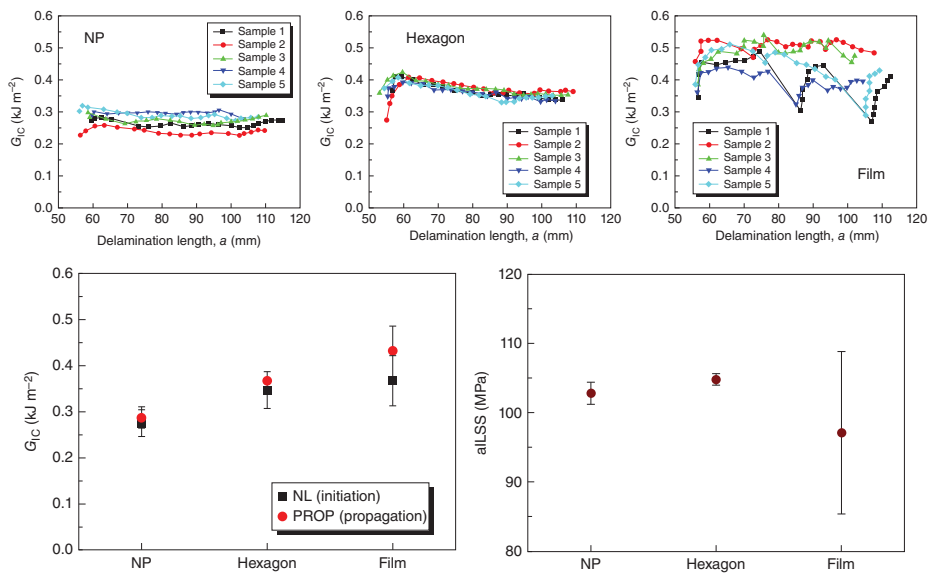


Figure 14.5 The top row shows G_{IC} comparisons between samples that were either nonprinted (NP), contained a printed hexagonal pattern (pattern 4 from Figure 14.3) of PMMA dots or a continuous film of PMMA. The bottom row compares crack initiation and propagation in the left-hand figure and the apparent interlaminar shear strength (aLSS), which is derived from the SBS test on the right side. In all cases $n = 5$. (Zhang *et al.* (2015) [18]. Reproduced with permission.)

the interleave approach whereby a film of toughening material is placed between the pre-preg sheets during lay-up. Figure 14.5 shows that the average $G_{Ic(\text{initiation})}$ and $G_{Ic(\text{propagation})}$ of the printed film samples are higher than that of the discrete dot system. However, the crack propagations of the printed film samples were unstable compared to that of the nonprinted control or the discrete dots. This instability introduces a large degree of variability, which is not ideal for industrial applications. The printed film is not efficient in terms of material usage either; eight times as much PMMA was printed compared to the discrete dot system. It is vital to minimize material usage since any increase in weight lessens the advantages of using carbon fiber composites in the first place.

Samples were also prepared for the SBS test, which provides values of aILSS. It can be seen from Figure 14.5 that the aILSS of printed film sample decreased by 5.5% compared to the control. However, the printed hexagon samples preserved the interlaminar strength compared to the control. The discrete dots in a hexagon pattern offer an increase in toughness but not at the detriment of increased variability or decreased shear strength. This result illustrates that inkjet printing appears to offer a clear benefit in enhancing the mechanical properties of carbon fiber composites.

Optimization of the hexagon pattern involved changing the dot spacing in X and Y . Two sets of samples were printed: in the first $dx = 0.4$ mm and $dy = 0.2$ mm, and in the second $dx = 0.7$ mm and $dy = 0.35$ mm. DCB testing was performed for both patterns and compared to the nonprinted control. Figure 14.6 shows that the $dx/dy = 0.4/0.2$ hexagon gave a highest value of G_{Ic} . The explanation is that this is a denser printing pattern and that the amount of PMMA per unit area has increased. Therefore, more energy is required to initiate and propagate a crack.

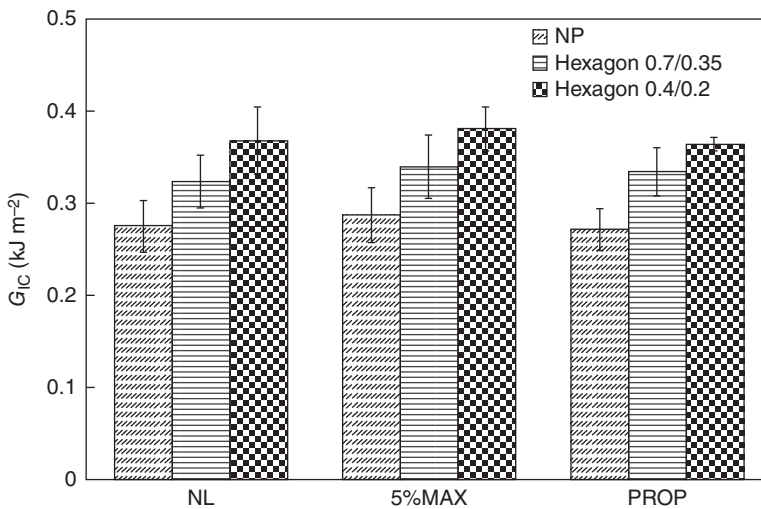


Figure 14.6 G_{Ic} comparison of nonprinted samples and samples that contain hexagons composed of PMMA dots. The two hexagon-patterned samples varied in the spacings in X and Y between the dots; $n = 5$ in all cases.

As a clear benefit can be seen from the exact printed pattern that is employed and from the density of dot pattern, the next obvious step is to vary the amount of PMMA that is deposited per droplet. This can be easily achieved by changing the concentration of the ink. Figure 14.7 shows the values of G_{IC} obtained for three sets of samples in which the concentration of PMMA was varied from 5% to 10% to 20%. The same hexagon printing pattern ($dx/dy = 0.4/0.2$) was used in all cases. A nonprinted control was also included. Figure 14.7 shows that the PMMA-containing specimens have higher values of G_{IC} compared to the control. However, an optimal value is seen at 10 wt% PMMA. The jump from 10% to 20% is greater than that from 5% to 10%, and it may be that higher values could be obtained for 15%, but 10% was deemed optimal since increasing ink concentration ultimately means increasing overall weight of the printed composite system.

An interesting application of the printed PMMA system can be seen in Figure 14.8. Two samples for DCB testing were prepared, in which one half of the sample contained the optimal print pattern ($dx/dy = 0.4/0.2$ and 10% PMMA) and the other half was unprinted. It can be seen from Figure 14.8 that the G_{IC} (fracture toughness) values of the PMMA printed areas are comparatively higher than those of unprinted areas. In Sample A, G_{IC} increases when the crack enters the printed region, whereas in Sample B G_{IC} decreases once the crack leaves the printed region. This experiment illustrates another advantage of using inkjet printing in this particular application area as property-graded materials can be produced, which means regions of increased toughness can be manufactured. Such an approach could be of interest to the machining of carbon fiber composites, where the limitation of cracks induced by machining is desirable.

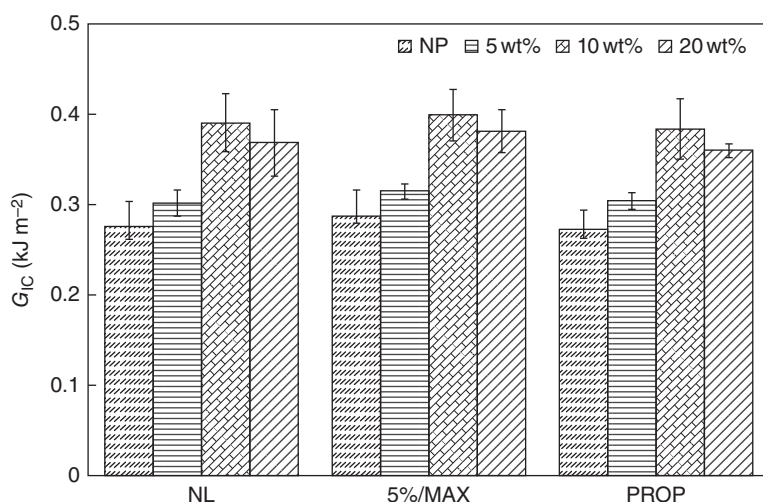


Figure 14.7 The measured values of G_{IC} for four composite samples. Three of the sample sets contained an inkjet-printed hexagon pattern of PMMA dots and varied only in the amount of PMMA that each dot contained. The fourth sample was a nonprinted (NP) control. In all cases, $n = 5$.

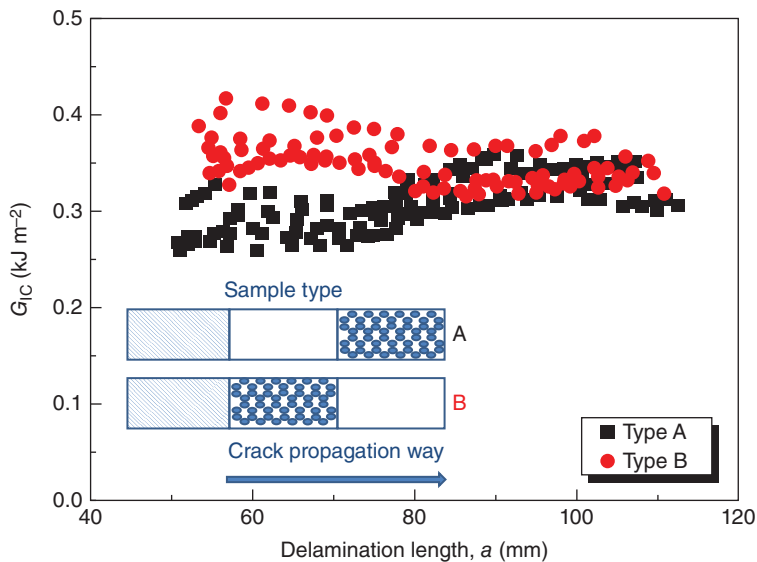


Figure 14.8 A graph showing how interlaminar fracture toughness can be locally tailored, in Sample A, a nonprinted region transitions into a printed toughened region, whereas in Sample B the opposite case occurs.

14.6 Carbon Fiber Composites that Contain Inkjet-Printed Patterns Composed of PMMA and PEG Microdroplets

One of the appeals of inkjet printing is its ability to deposit more than one ink. In graphics, this allows the user to deposit up to four different colored inks and combine them with the color of the substrate to create a vast range of shades and hues. In the research context, it means that two reactants can be printed to form a product *in situ*, an approach known as reactive inkjet printing [19]. A printed hexagon pattern in which each vertex of the hexagon contains a droplet of PMMA has been shown to toughen carbon fiber composites, but inkjet printing opens the way to produce multimaterial systems that could possibly offer multifunctional benefits. The first step down this path involved the printing of the optimal hexagon pattern but replacing three of the six dots with a different material. Figure 14.9 shows the print pattern that was used.

PEG was used as the second ink as this system had been investigated earlier [20]. Although the carbon fiber composites that contained inkjet-printed PEG showed a small increase in toughening, it was not as dramatic as that seen for PMMA. However, as PEG was the second most examined system, it was sensible to use it as the second component in the first multimaterial printed systems. After printing the optimal dx/dy 0.4/0.2 hexagon using 10% PEG and PMMA inks, samples were prepared for DCB testing, with the results shown in Figure 14.10. The dual material system exhibited a value of toughening efficiency similar to that of the single material PMMA system. This is a fascinating result as the amount of

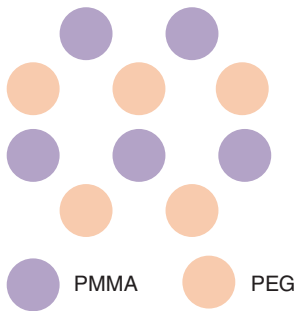


Figure 14.9 For multimaterial systems, a standard hexagonal pattern was employed, in which half of the dots were composed of a second material. In this particular case, PEG replaced half of the PMMA droplets. Dot spacing was $dx/dy = 0.4/0.2$ mm, and the concentration of the ink was 10% in both cases. (Zhang *et al.* (2015) [18]. Reproduced with permission.)

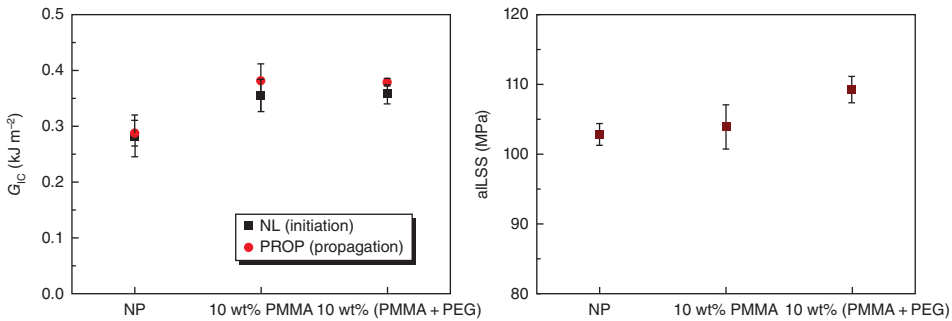


Figure 14.10 The values of G_c and aLSS measured for three sample sets. One of the sample sets was the nonprinted (NP) control, the second was the optimized PMMA single material system, and the third was a dual material PMMA/PEG system. (Zhang *et al.* (2015) [18]. Reproduced with permission.)

PMMA per unit area has effectively been halved. The exact explanation for this observation is not yet clear, although the next section offers some thoughts as to what the toughening mechanisms may be. The second, and even more surprising, result is the increase in the interlaminar shear strength of the dual material system. Although the 5% increase is not dramatic, it is significant; note that the lowest value of aLSS for the dual material system is greater than that of the highest value of the nonprinted control. It should be remarked upon that a corresponding decrease of 5% would definitely been seen as detrimental. At the time of writing, the only conclusion to make was that this area of multimaterial printing (and possibly multifunctional composites) has provided some interesting results and suggests a fruitful research direction to explore.

14.7 Morphology of the Printed PMMA and PEG Droplets

The increase in toughening for the printed PMMA system and the dual material PMMA/PEG system has not yet been elucidated. However, a set of experiments were performed for providing a deeper understanding of what form the printed material takes in the final composite system. Samples were prepared using microscope glass slides that had been coated with a layer of epoxy resin

(CYCOM®977-20 RTM, Cytec Engineered Materials Ltd., UK). The coated slides were exposed to a “pre-cure” step to mimic the resin state in the pre-preg sheet. The pre-cured slides were then used as substrates with either PMMA or PEG droplets inkjet printed upon them. After printing, the samples were left to dry at room temperature for at least 1 h before a second pre-cured epoxy-coated slide was placed on top, forming a sandwich structure. The samples were then heat treated for 30 min at 160 °C, which imitated the curing cycle that the final printed composites would experience. Optical microscopy was used to examine the samples in two stages: the first was before heating and before being covered with the second coated slide and the second was after the final heating step. A film of PMMA and lines of PMMA were also printed.

Figure 14.11 shows the morphologies of the PMMA droplets, before and after heating. It can be seen (Figure 14.11b) that the PMMA droplets in the hexagon pattern formed micro-sized particles, or beads, that were embedded in the epoxy resin after heating. It should be noted that the printed pattern was retained although the size increased slightly due to the liquid nature of the epoxy resin during heating and the nonporous nature of the glass slides. The diameter of the PMMA beads was measured to be $\sim 37\ \mu\text{m}$, with a small degree of variation. The other two printed structures behaved differently. The film broke up into a disordered array of beads that exhibited a wide range of diameter sizes (Figure 14.11d). The printed lines showed a similar breakdown, although the overall line structure was roughly maintained (Figure 14.11f).

As can be seen from Figure 14.12, the morphology of the PEG droplets differed considerably from that of the PMMA, exhibiting a high degree of miscibility with the epoxy resin after heating. Before heating, the PEG droplets appeared as beads, which is likely to be a consequence of incompatibility of the solvent with the epoxy. The inkjet-printed PEG droplets did not bead up and shrink with

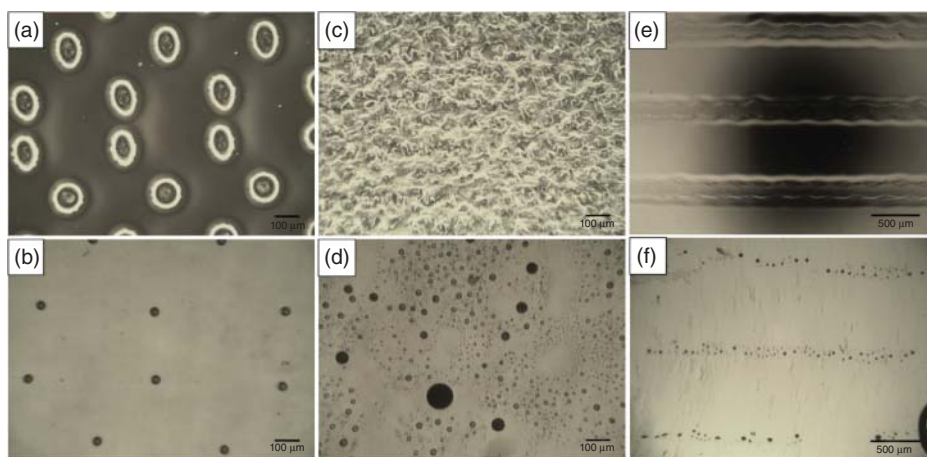


Figure 14.11 The morphologies of inkjet-printed PMMA droplets that were embedded into epoxy resin, which had been coated on glass slides. Three structures were printed: hexagon, film, and lines; and the droplet morphologies are shown both before (a,c,e) and after heating; (b,d,f). (Zhang *et al.* (2015) [18]. Reproduced with permission.)

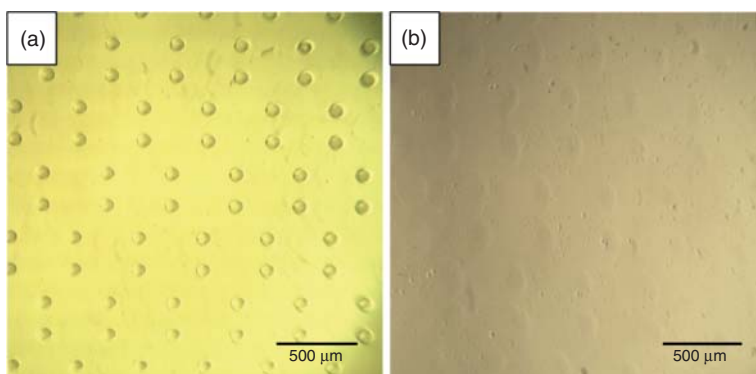


Figure 14.12 Morphology of PEG droplets embedded in epoxy resin (a) before heating and (b) after heating. (Zhang *et al.* (2015) [18]. Reproduced with permission.)

heating, rather it seems as though a barely visibly pancake resembling the original printed droplet is formed, which suggests that the PEG did not completely diffuse into the whole resin but localized PEG-rich regions in the bulk epoxy.

14.8 Printed Polymers for Intrinsic Repair of Composites

As mentioned at the start of this chapter, the lower fracture toughness of composites compared to their metallic competitors coupled with the difficulty in detecting and assessing damage has caused concerns. As a consequence, a large amount of research has been directed toward nondestructive testing of composites and embedding self-sensing systems [21–23]. One approach has been to distribute monomers that are capable of undergoing thermally reversible cross-linking via Diels–Alder chemistry. Thermally reversible polymers are of interest as the reversibility of polymers based on main chain or pendant Diels–Alder moieties is well established [24]. Following the work that involved printing PMMA, which led to tougher composites and a dual material PEG/PMMA system that appears to be both tougher and stronger, the work discussed in this section focuses on the inkjet printing of a monomer solution that introduces a repairing ability to the carbon fiber composite.

The specific monomers were synthesized using a modified scheme (Figure 14.13) based on the work of Murphy *et al.* [26]. The starting molecule is dicyclopentadiene, which exists in a thermal equilibrium with two equivalents of cyclopentadiene. The full details of this synthesis have been reported by Fleet *et al.* [25] and lie outside the scope of this chapter. A series of synthetic steps are performed, which resulted in two monomer structures (Structures 5 and 6 in Figure 14.13); the difference between the monomers is an intrachain atom that is either an oxygen (called monomer 401, Structure 6) or a carbon (monomer 400, Structure 5).

After the monomer was synthesized, a 5% w/v ink was formulated using ethyl acetate as the solvent. The *Z* number of the ink was calculated to be 79.8, which

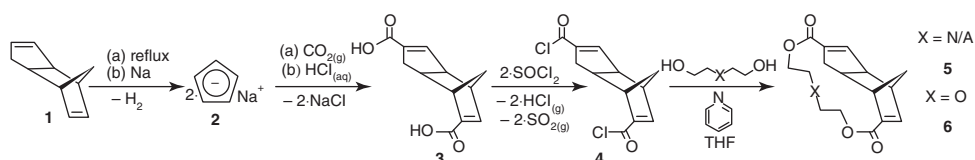


Figure 14.13 The synthesis route employed for producing monomers that can introduce a repair ability into the carbon fiber composites. The scheme is based on that first reported by Murphy *et al.* [13]. (Fleet *et al.* (2015) [25]. Reproduced with permission of Royal Society of Chemistry.)

is significantly higher than the upper limit of printability of 10 that was determined by Reis and Derby [27]. However, other researchers have commented on successfully printing high Z number inks [28]; in this case, it was found that after optimization, satellite droplets were not a problem. The monomer inks were successfully printed onto carbon fiber-epoxy pre-preg using the optimal hexagon pattern ($dx/dy = 0.4/0.2$), which was then prepared into the final carbon fiber composite test specimens for SBS testing. Four experimental samples were prepared: unprinted control, 1% M400, 5% M401, and 5% M400. The amount of monomer synthesized was small, which is why a 1% ink was produced. In the case of both of the 5% samples, the inner four plies of a total of eight plies were printed. For the 1% M400 samples, all plies were printed.

The mean results are shown in Table 14.1. The samples containing the 5% ink exhibited a significantly higher aILSS compared to the control and the sample containing the 1% M400 droplets. There was no significant difference between the two 5% samples, and no significant difference was observed between the 1% sample and the control.

After the initial testing, the SBS specimens were subjected to a thermal healing cycle (180°C , 6 h) and then retested. The results, shown in Figure 14.14a, indicate that no sample set fully recovered in terms of interlaminar shear strength. However, the sample sets that contained the 5% M400 ink and the 5% M401 showed a greater recovery compared to the nonprinted control and the 1% test specimens. Greater recovery could possibly be gained with increased concentration of monomer.

Table 14.1 Apparent interlaminar shear strength (aILSS) of the printed and unprinted control composite samples as determined by short beam method.

Sample	Number of samples tested	aILSS (MPa)
Nonprinted control	7	104.61 ± 2.26
1% M401 (8 ply printed)	8	106.18 ± 4.00
5% M401 (4 ply printed)	9	114.96 ± 3.28
5% M400 (4 ply printed)	10	115.60 ± 3.44

Fleet *et al.* (2015) [25]. Reproduced with permission of Royal Society of Chemistry. Given error is 1 std. dev.

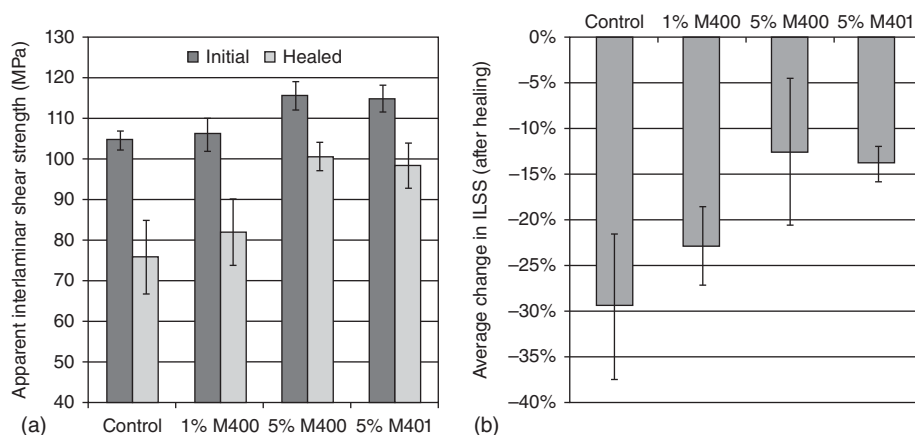


Figure 14.14 (a) Apparent interlaminar shear strength (aILSS) results obtained from the short-beam method for printed samples and unprinted controls before and after a thermal repair cycle. (b) The average percentage reduction in aILSS after a thermal healing cycle shown for printed and unprinted samples. All error bars shown are 1 std. dev. (Fleet *et al.* (2015) [25]. Reproduced with permission of Royal Society of Chemistry.)

14.9 Conclusions

Carbon fiber composite materials are being increasingly used for structural applications on account of their high strength to weight ratio. However, a drawback of carbon fiber composites is their brittleness and their tendency to hide signs of cracking or fatigue. Approaches that address these drawbacks must take into account the existing benefits of composites, which means any additional weight must be kept at a minimum and the solution must not improve one mechanical property at the expense of a second (e.g., increasing toughness must not, ideally, be accompanied by a decrease in interlaminar shear strength).

Inkjet printing offers great potential in terms of addressing this demand of maintaining weight while increasing mechanical performance. Inkjet's ability to tailor droplet volumes and high levels of reproducibility mean that it can print an array of droplets onto carbon fiber pre-preg sheets, which are then used for final manufacture. By producing an ordered hexagon of discrete, uniform PMMA droplets, the interlaminar fracture toughness (G_{Ic}) was seen to increase by 40%. The overall weight increase in the composite system has been calculated as 0.02% [29]. The pattern has been shown to have an influence. When PMMA amount per unit area was kept constant but the pattern was varied from a hexagon to a square to lines, the hexagon gave the highest increase in G_{Ic} .

The degree of surface coverage has an influence with the larger surface coverage yielding better results; however, taking this approach to its extreme where all of the surface is covered results in a disordered array of droplets that are both randomly sized and positioned. Although G_{Ic} was higher for the printed film, there was a large degree of variation in the measurements and the interlaminar shear strength was seen to be decreased. Increasing the amount of PMMA per droplet was seen to have a beneficial effect up to 10%, where after a decline was seen once

20% was used. A potentially useful demonstration of inkjet printing's use lies in the production of functionally graded composites, which can produce regions of increased toughness. This may be of use to engineers who wish to machine composite materials, since the localized toughening could inhibit the spread of cracks caused by machining processes such as drilling.

Inkjet printing allows a user to deposit more than one material, which in the context of this chapter opens up the possibility of producing multifunctional, multimaterial composites. Initial work in this area investigated a dual material system that deposited 50% PMMA droplets and 50% PEG droplets into the optimal hexagon pattern. The results showed that the increase in toughening was maintained and a small increase in interlaminar shear strength was obtained. This work is still in its early stages, but suggests strongly that inkjet's ability to deposit more than one material onto a single layer could be of tremendous appeal.

The final section of the chapter discussed the printing of monomer-containing inks that exploit the Diels–Alder reaction to initiate repair of a damaged composite once exposed to heat treatment. After a thermal treatment specimens were retested using SBS, it was found that the samples that had been printed with 5% monomer inks had recovered a greater amount of the initial properties before damage.

Acknowledgments

The authors would like to acknowledge the support given by the European Office of Aerospace Research and Development and the U.S. Army Research, Development and Engineering Command's Forward Element for their support, both financial and advisory.

References

- 1 Madec, M.B., Smith, P.J., Malandraki, A., Wang, N., Korvink, J.G., and Yeates, S.G. (2010) Enhanced reproducibility of inkjet printed organic thin film transistors based on solution processable polymer-small molecule blends. *J. Mater. Chem.*, **20**, 9155–9160.
- 2 Smith, P.J., Shin, D.-Y., Stringer, J.E., Derby, B., and Reis, N. (2006) Direct ink-jet printing and low temperature conversion of conductive silver patterns. *J. Mater. Sci.*, **41**, 4153–4158.
- 3 Sanchez-Romaguera, V., Ziai, M.A., Oyeka, D., Barbosa, S., Wheeler, J.S.R., Batchelor, J.C., Parker, E.A., and Yeates, S.G. (2013) Towards inkjet-printed low cost passive UHF RFID skin mounted tattoo paper tags based on silver nanoparticle inks. *J. Mater. Chem. C.*, **1**, 6395–6402.
- 4 Zhang, Y., Tse, C., Rouholamin, D., and Smith, P.J. (2012) Scaffolds for tissue engineering produced by inkjet printing. *Cent. Eur. J. Eng.*, **2**, 325–335.
- 5 Soutis, C. (2005) Carbon fiber reinforced plastics in aircraft construction. *Mater. Sci. Eng., A*, **412**, 171–176.
- 6 Garg, A.C. (1998) Delamination: A damage mode in composite structures. *Eng. Fract. Mech.*, **29**, 557–584.

- 7 Arguelles, A., Viña, J., Canteli, A.F., and Bonhomme, J. (2009) Fatigue delamination, initiation, and growth, under mode I and II of fracture in a carbon-fiber epoxy composite. *Polym. Compos.*, **31** (4), 700–706.
- 8 Veedu, V.P., Cao, A., Li, X., Ma, K., Soldano, C., Kar, S., Ajayan, P.M., and Ghasemi-Nehjad, M.N. (2006) Multifunctional composites using reinforced laminae with carbon-nanotube forests. *Nat. Mater.*, **5**, 457–462.
- 9 Mukhopadhyay, S.M. and Karumuri, A.K. (2010) Nanotube attachment for prevention of interfacial delamination. *J. Phys. D: Appl. Phys.*, **45**, 365301.
- 10 Lee, S.-H., Kim, H., Hang, S., and Cheong, S.-Y. (2012) Interlaminar fracture toughness of composite laminates with CNT-enhanced nonwoven carbon tissue interleave. *Compos. Sci. Technol.*, **73**, 1–8.
- 11 Dry, C. (1996) Procedures developed for self-repair of polymer matrix composite materials. *Compos. Struct.*, **35**, 263–269.
- 12 Hayes, S.A., Jones, F.R., Marshiya, K., and Zhang, W. (2007) A self-healing thermosetting composite material. *Composites A*, **38** (4), 1116–1120.
- 13 Hedrick, J.L., Yilgor, I., Wilkes, G.L., and McGrath, J.E. (1985) Chemical modification of matrix Resin networks with engineering thermoplastics. *Polym. Bull.*, **13**, 201–208.
- 14 Pingkarawat, K., Wang, C.H., Varley, R.J., and Mouritz, A.P. (2012) Self-healing of delamination fatigue cracks in carbon fibre–epoxy laminate using mendable thermoplastic. *J. Mater. Sci.*, **47** (10), 4449–4556.
- 15 Sela, N. and Ishai, O. (1989) Interlaminar fracture-toughness and toughening of laminated composite- materials - a review. *Composites*, **20**, 423–435.
- 16 BS EN ISO 14130:1998 (1998) Fibre-reinforced plastic composites. Determination of apparent interlaminar shear strength by short-beam method. British Standards Institute.
- 17 BS EN ISO 15024:2001 (2001) Fibre-reinforced plastic composites – determination of mode I interlaminar fracture toughness, GIC, for unidirectionally reinforced materials. British Standards Institute.
- 18 Zhang, Y., Stringer, J., Hodzic, A. and Smith P.J. (2015) *Elaborating Printing Parameters in Using Inkjet Printing to Toughen Carbon Fibre Reinforced Plastic Composites*. Proceedings of the 20th International Conference on Composite Materials, Copenhagen, July 19-24/2015 Copenhagen.
- 19 Smith, P.J. and Morrin, A. (2012) Reactive inkjet printing. *J. Mater. Chem.*, **22**, 10965–10970.
- 20 Zhang, Y., Stringer, J., Grainger, R., Smith, P.J., and Hodzic, A. (2014) Improvements in carbon fibre reinforced composites by inkjet printing of thermoplastic polymer patterns. *Phys. Status Solidi RRL*, **8** (1), 56–60.
- 21 Amenabar, I., Lopez, F., and Mendikute, A. (2013) An introductory review to THz non-destructive testing of composite mater. *J. Infrared, Millimeter, Terahertz Waves*, **34**, 152.
- 22 Shubel, P.J., Crossley, R.J., Boateng, E.K.G., and Hutchinson, J.R. (2013) Review of structural health and cure monitoring techniques for large wind turbine blades. *Renewable Energy*, **51**, 113.
- 23 Swait, T.J., Jones, F.R., and Hayes, S.A. (2012) A practical structural health monitoring system for carbon fibre reinforced composite based on electrical resistance. *Compos. Sci. Technol.*, **72**, 1515.

- 24 Pratama, P.A., Sharifi, M., Peterson, A.M., and Palmese, G.R. (2013) Room temperature self-healing thermoset based on the Diels–Alder reaction. *ACS Appl. Mater. Interfaces*, **5**, 12425.
- 25 Fleet, E.J., Zhang, Y., Hayes, S.A., and Smith, P.J. (2015) Inkjet printing of self-healing polymers for enhanced composite interlaminar properties. *J. Mater. Chem. A*, **3**, 2283–2293.
- 26 Murphy, E.B., Bolanos, E., Schaffner-Hamann, C., Wudl, F., Nutt, S.R., and Auad, M.L. (2008) Synthesis and characterization of a single-component thermally remendable polymer network: Staudinger and Stille revisited. *Macromolecules*, **41**, 5203.
- 27 Reis, N. and Derby, B. (2002) Ink jet deposition of ceramic suspensions: Modeling and experiments of droplet formation. *MRS Online Proc. Libr.*, **2000**, 625. doi: 10.1557/PROC-625-117
- 28 Perelaer, J., Smith, P.J., van den Bosch, E., Grootel, S.S.C., Ketelaars, P.H.J.M., and Schubert, U.S. (2009) The spreading of inkjet-printed droplets with varying polymer molar mass on a dry solid substrate. *Macromol. Chem. Phys.*, **210**, 495–502.
- 29 Zhang, Y., Stringer, J., Grainger, R., Smith, P.J., and Hodzic, A. (2014) Fabrication of patterned thermoplastic microphases between composite plies by inkjet printing. *J. Compos. Mater.* doi: 10.1177/0021998314533715

15

Inkjet-Printable Nanomaterials and Nanocomposites for Sensor Fabrication

Niamh T. Brannelly and Anthony J. Killard

15.1 Introduction

Sensors are an essential part of daily life, lending their use to automotive safety, health, and security alarms and detectors. These applications often require inexpensive, single-use devices, which are suited to inkjet printing of nanomaterials. Nanomaterials utilized for the production of printed devices have been reviewed elsewhere [1], as has fabrication options for biosensor and biodevice production [2]. The particle size should be less than 100th the size of the inkjet print cartridge nozzle. Nanoparticles should also have a narrow distribution of sizes and be homogeneously distributed throughout the solution to ensure good jetting [3]. Perhaps the most important consideration when inkjet printing nanomaterials is their dispersivity in solution. This is an essential parameter in avoiding agglomeration and blockage of the cartridge nozzles. Rheological properties such as ink viscosity, surface tension, density, temperature, humidity, pH, and nozzle diameter are also important considerations. They all influence the spreading of the liquid drops, which affect the inkjetted film formation. Inkjet printing requires an ink that is ~ 10 cP viscosity [4]. Formulations have been employed in the processing of nanomaterial inks to achieve ideal print properties. These typically involve addition of other constituents such as dispersants, adhesion promoters, surfactants, thickeners, stabilizing agents, and other additives [5]. Subsequent to printing, sintering is carried out to remove these constituents in order to achieve sufficient film conductivity. This process is prone to ink cracking or peeling off the substrate upon drying. Oxidation and longevity of the inks developed and deposited are also important considerations [1].

A wide variety of inkjet-printed nanomaterials have been explored in the literature for sensor production. These materials may be used to fabricate the electrode material or the active sensing layer. These materials have been divided into the following categories for discussion throughout this chapter: metallic, polymers, and carbon materials. It is common to combine any of these materials to form nanocomposites, which may also be inkjet-printed for sensing applications. This chapter gives an overview of nanomaterial ink synthesis and properties. Examples of sensors and devices fabricated by inkjetting these nanomaterials are also described.

15.2 Metallic Inks

Metallic “nanoinks” are widely used and are commercially available. The conductivity of nanoparticle materials is comparable (albeit lower) with that of the bulk material. They are also less likely to oxidize and clog the inkjet printhead than bulk [6]. Inkjet printing has been used to deposit gold [7–12], silver [13–19], copper [20–24], nickel [21, 22, 25], and alumina [26–28]. Gold and silver dominate this field, but they are expensive materials and so metals such as copper and nickel are preferable. However, they tend to oxidize, which may affect their conductivity and lifetime [29].

Metallic nanoparticles may be suspended in water or an organic solvent (toluene, ethylene glycol, cyclohexane), which readily evaporates upon deposition. They are prone to agglomeration in solvents, which leads to clogging of print cartridge nozzles. Polymer and surfactant coatings along with functionalization of the metallic surface have been employed to prevent agglomeration of the nanoparticles. These prevention measures reduce the conductivity of the metallic film and so high-temperature sintering is required to remove them. This makes them unsuitable for use with plastic substrates. Nanoparticles have a high surface area, which lowers the sintering temperatures compared to the bulk material. For example, gold nanoparticles are sintered at 300–500 °C, but the bulk is sintered at 1063 °C [5]. As a low temperature alternative, photonic or flash microwave sintering may be combined with thermal sintering.

15.2.1 Gold

Gold is widely used as a metal for sensor applications because of its chemical inertness and processability. Stable gold nanodispersions can be prepared by the reduction of gold chloride (AuCl_3) with reducing agents such as sodium borohydride (NaBH_4) or citric acid in the presence of a protecting ligand. This forms an electrostatic repulsion between particles and thus prevents agglomeration [30]. Gold nanoparticles are often alkanethiol capped via sulfur chemisorptions onto the gold surface. This is implemented by adding thiols that contain an amine or carboxyl group into the reduction process. Easy modification of the particles using thiol compounds make them very attractive for immobilization or capture applications such as electrochemical immunosensors. An example of this is the formation of an affinity biosensor, where alternate layers of biotin/streptavidin/biotinylated C-reactive protein (CRP)-antigen/anti-CRP antibody were grown on inkjet-printed gold electrodes deposited onto disposable paper substrates (Figure 15.1). This impedimetric platform provides a route for fabricating inexpensive, recyclable, point-of-care diagnostic devices [31].

Another biosensing example of inkjet-printed gold nanoparticles was reported by Jensen *et al.* [9]. Gold nanoparticle ink was printed onto a flexible, heat-resistant polyimide Kapton substrate and subsequently sintered to create eight-electrode arrays. The costing of this platform was <€0.20 per array. The inkjet-printed working electrodes had reproducible surface areas with an RSD of <3%. Capture antibodies for IL-6 were linked onto the eight-electrode array and used in sandwich immunoassays. A biotinylated secondary antibody with 16–18

Figure 15.1 Schematic diagram of the supramolecular protein layers streptavidin, biotinylated C-reactive protein (CRP) antigen, and the bound analyte (anti-CRP antibody) grown on biotinylated self-assembly monolayer (SAM)-covered printed gold electrodes on a paper substrate [31]. (Ihalainen *et al.* (2013) <http://www.mdpi.com/2079-6374/3/1/1/htm>.)

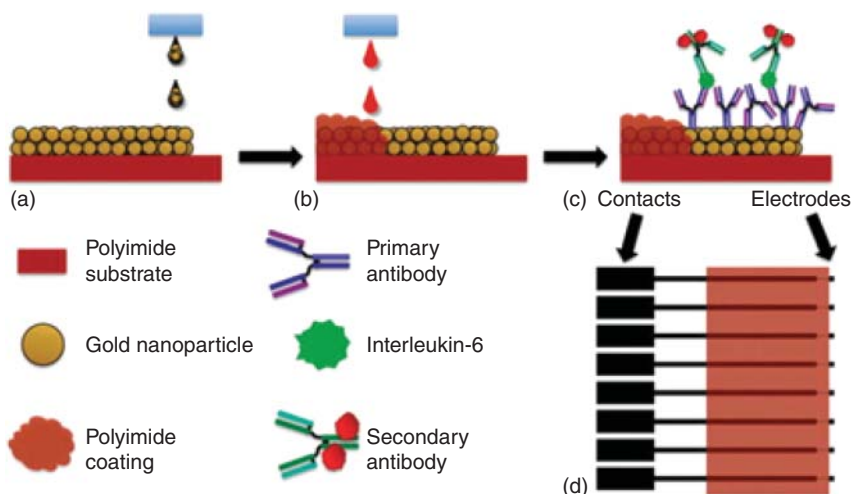
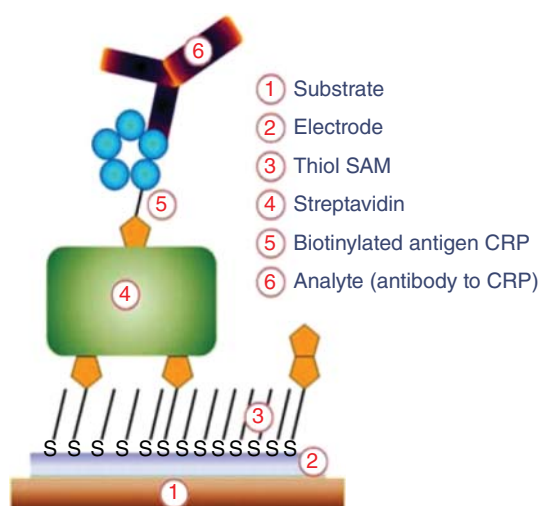


Figure 15.2 Fabrication of gold nanoparticle arrays: (a) inkjet printing of the gold nanoparticle ink onto the polyimide substrate; (b) inkjet printing the poly(amic acid) ink to insulate the electrode leads; (c) building the immunoassay for electrochemical detection of human IL-6; (d) the gold nanoparticle pattern (black) shown overlaid with the poly(amic acid) printed pattern (orange). (Jensen *et al.* (2011) [9]. Reproduced with permission of Royal Society of Chemistry.)

horseradish peroxidase (HRP) labels was used, and detection was achieved by hydroquinone-mediated amperometry (Figure 15.2). The arrays provided a clinically relevant detection limit of 20 pg ml^{-1} in calf serum, sensitivity of $11.4 \text{ nA pg}^{-1} \text{ cm}^{-2}$, and a linear dynamic range of $20\text{--}400 \text{ pg ml}^{-1}$ [9].

Inkjet-printed three-electrode systems have also been fabricated on a coated paper substrate for glucose sensing. Inkjet-deposited gold nanoparticles formed the working and counter-electrodes, while the quasi-reference electrode was formed using inkjet-printed silver nanoparticles electrochemically transformed to silver/silver chloride (Ag/AgCl) via chlorination. This

platform was then used as a potentiometric pH sensor across the range of 2–10 with sensitivity close to -59 mV per pH unit [32]. This platform was then used to electropolymerize polyaniline and glucose oxidase (GO)-entrapped poly(3,4-ethylenedioxythiophene) (PEDOT) films for use as an amperometric sensor for glucose. This work demonstrated a low cost ($\text{€}0.04$ per cm^2), multiapplication paper sensing platform.

Gold nanoparticles have also been used in the gas- and vapor-sensing arenas. An example of this is a low-cost, paper-based electrochemical oxygen sensor. This sensor was fabricated using diluted gold nanoparticles inkjet-printed onto a mixed cellulose ester membrane. It has been demonstrated that dilute gold nanopatterns can achieve required conductivities by self-catalytic growth using HAuCl_4 . Two hundred electrode arrays were produced in 30 min of printing and 2 h of Au growth. Oxygen determination was reported over the linear range of 0.054–0.177 v/v%, along with a low detection limit of 0.0075% and a short response time of less than 10 s [33]. The addition of *N*-methyl-2-pyrrolidone (NMP) to water was shown to improve dispersivity of gold nanoparticles. This two-solvent system has been used to functionalize gold nanoparticles with 1-hexanethiol in order to provide a hydrophobic sensing layer. The performance of 1-hexanethiol-functionalized gold nanoparticle chemiresistor sensors used for the impedimetric detection of toluene, dichloromethane, and ethanol has been assessed and reported [8].

15.2.2 Silver

Silver is cheaper than gold and is, therefore, the most commonly used metal to fabricate devices and electronics. Silver nanoparticle conductive inks have been employed for a very long time in the preparation of inkjet-printed sensors. As with gold, silver nanodispersions are synthesized in the presence of organic by reduction of silver nitrate (AgNO_3) by NaBH_4 . Solvents decrease the conductivity of the films and so they are removed by sintering at high temperatures. Upon sintering, the nanoparticles will fuse together forming continuous, conductive paths. Thermal behaviors of inkjet-printed metallic films have been investigated. It was shown that silver nanoparticulate films became highly conductive ($\sim 3.2 \mu\Omega$) when heated at 200°C [14]. In order to reduce processing of the mass producible sensors, a spontaneous solvent evaporation process at room temperature is an attractive option. This has been carried out by inkjet printing silver nanoparticles, which possess a positive charge along with a negatively charged stabilizer (polyacrylic acid sodium salt), which resulted in a net neutral charge. The neutral charge incurred a spontaneous sintering process at room temperature [34].

The fabrication of humidity sensors has employed inkjet-printed silver nanoparticles. Examples of this application have been presented in the literature on plastic [35] and paper [19] substrates.

15.2.3 Copper, Nickel, and Alumina

Copper has gained a lot of attention as a cheap alternative to gold and silver inks. It is just 6% less conductive than silver [36]. However, the tendency of copper

to aggregate and oxidize is more common than gold or silver. If copper were to be fabricated in such a way that did not oxidize, it would make it a low cost and effective sensor. Strategies to combat oxidation of copper have been developed and reported in the literature. These involve coating them with a protective layer such as organic polymers, surfactants, carbon-based materials, silica, or metals. These are discussed in detail in a review paper on the topic of printed copper nanoparticles for electronics [36].

The most convenient and traditional route to synthesizing copper nanoparticles is based on the reduction of the metal. Copper nitrate ($\text{Cu}(\text{NO}_3)_2$) is reduced by hydrazine hydrate excess in the presence of polyacrylic acid sodium salt as a polymeric stabilizer [36]. The excess of hydrazine prevents oxidation of the copper nanoparticles in the aqueous dispersion if kept in closed vials. The excess hydrazine is then washed out and silver salt is added. These oxidation-stable copper–silver nanoparticles have been successfully inkjet-printed and evaluated [37]. Antioxidants have also been employed for copper nanoparticles to prevent oxidation and loss of conductivity [38]. This has seen quick (5 min) synthesis by utilizing a modified polyol process with slightly soluble $\text{Cu}(\text{OH})_2$ as precursor, L-ascorbic acid as the reductant, and polyethylene glycol (PEG)-2000 as the protectant. They did not suffer significant oxidation after being stored for 30 days in ambient conditions.

Inkjet printing of copper nanoparticles has been demonstrated in the literature with reports of uniform, small droplets ($110 \pm 2 \mu\text{m}$) in continuous thin lines ($500 \pm 10 \mu\text{m}$) using electrohydrodynamic atomization inkjet printing [39]. Conductive copper and nickel lines have been inkjet-deposited onto paper. The inks were prepared as follows. For copper printing, a 1.25 M CuSO_4 and sodium citrate solution was prepared. For nickel line printing, a 2.5 M NiSO_4 solution was prepared as the nickel ink. Sodium borohydride was added as the reducing agent along with citrate to stabilize the inks. The best conductivity of printed copper lines is $1.8 \times 10^6 \text{ S m}^{-1}$ and that of nickel is $2.2 \times 10^4 \text{ S m}^{-1}$, about 1/30 and 1/600 of their bulk metal counterparts, respectively [22]. Inkjet printing has also been employed to deposit a layer of copper and nickel–phosphorus onto polyethylene naphthalate (PEN) substrates. The electrical resistivity of deposited nickel–phosphorus and copper layers was $3.8 \pm 0.2 \text{ m}\Omega \text{ cm}^{-1}$ and $29 \pm 2 \mu\Omega \text{ cm}^{-1}$, respectively [21].

A systematic procedure for inkjet printing of aluminum oxide (Al_2O_3) nanoparticles in rectangular straight microchannels using water-based inks to generate support layers for gas-phase catalytic reactions has been reported. The significance of co-solvent and hydro-soluble polymer on ink formulation, drop formation, the piezoelectric activation parameters optimization, droplet impact, and minimum standoff distance was studied. The effect of ink composition on the shape of the alumina film formed after drying in the microchannels was investigated as well [39].

15.2.4 Metal Oxides

Metal oxides may be processed into inkjet-printable formulations using colloidal suspensions or sol–gel chemistries. Semiconducting metal oxides have diverse

applications in a range of sensing arenas such as automotive exhausts, household alarms, healthcare, and industrial and safety processes [40]. Colloidal suspensions of metal oxides are prone to aggregation. Surfactants and polymers may be added to prevent this. They may be removed subsequently by heat treatment ($>300^{\circ}\text{C}$) or microwave flash method. Nonionic amphiphiles (wetting properties and effective stabilizer) and ethylene glycerol (used as binder to control viscosity) may also be added to alter the properties of the ink such as viscosity, which also affects printability. An acid such as hydrochloric, polyacrylic, carboxylic, or acetic acid may be added to maintain the pH of the ink and ensure the surface charge of the metal oxides [41]. The majority of metal oxide nanoparticles being printed utilize solvent-based solutions, which minimize cracking or damage during the drying and sintering stage [42]. They typically use alcohols (ethanol, methanol, and isopropanol) along with a dispersative agent to enhance dispersion and prevent aggregation. This method is prone to aggregation, so colloidal nanoparticles as precursors based on sol–gel chemistries are recommended for metal oxide nanoparticulate inks. Sol–gel layers are porous agglomerates of nanoparticles. The process involves a homogenous solution of metal precursors (metal alkoxides) in an organic solvent- or water-based solution. This solution is then converted into a printable colloidal nanoparticle sol ink by treatment with a reagent such as acid, base, and ligands. Then, this is inkjet-printed forming a thin gel film, which is then dried to form the oxides. The most important step in the sol–gel process is the rate of the metal precursor formation, which if left to continue may cause agglomeration. Another issue is hydrolysis and/or condensation of the gels. This may cause phase separations and effect sensing properties.

Inkjet-printed metal oxide nanoparticles (WO_3 , SnO_2 , and ZnO) are renowned for gas sensing because they offer rapid responses, high sensitivity, and good stability. They have been employed to sense atmospheric and industrial gases such as CO , CH_4 , H_2 , ethanol, and H_2S . Prepared nanometer-scale WO_3 nanoparticles decorated with metals (Ag, Pt, and Pd) are suspended in water and have been inkjet-printed for gas-sensing (H_2 , NO , H_2S , and CO) applications down to $\sim 0.1\%$ of their concentrations in air [40]. The low waste way of processing the sensor via inkjet printing spurred the authors to calculate material costs. They concluded that by combining inkjet deposition with low cost substrates, the majority of the expense would be due to measurement electronics as opposed to sensing materials. The device would cost no more than 1 euro per 1 million devices.

15.3 Conductive Polymers

Metallic inks are excellent conductors and are widely used in sensor technology where sensitive, accurate, and precise measurements in complex matrices are required. However, sensitivity and cost must be balanced. For this reason, research is ever increasing in the field of printed organics, which have the potential to replace metallic inks. They are inexpensive and environmentally friendly. They can behave as both conductors and semiconductors. Conducting polymers have been employed as sensors to determine a range of analytes such

as toxic gases, organic compounds, and biological species [43]. This is due to their unique optical and electrical properties derived from the presence of a conjugated π -electron system present throughout the polymer backbone, which gives them their conducting properties. Conductive polymers such as polyaniline, polypyrrole, Prussian blue, and PEDOT have been combined with inkjet print technologies for sensor production. The most common method to do this is to synthesize polymer nanoparticles. Polymer nanoparticles are easily dispersed in aqueous solutions and can be paired with inkjet printing to produce the sensing films. However, polymer inks have lower conductivity than their metallic counterparts and are known to exhibit non-Newtonian behaviors [44]. This affects inkjet deposition of the inks and may cause tailing when the ink is ejected from the cartridge nozzle, which often results in splashing of the ink upon contact with the substrate. They are also susceptible to changes due to humidity and atmospheric gases.

15.3.1 Polyaniline

Polyaniline (emeraldine salt) is one of the most promising conducting polymers in the sensing arena. It has high conductivity, optical properties, and good environmental stability. It is insoluble in water, so inkjet printing was not an option until polyaniline nanoparticles were produced via micellar polymerization [45]. This process polymerizes aniline in the presence of an oxidant (ammonium persulfate (APS)) in a surfactant (dodecylbenzene sulfonic acid (DBSA)) micellar solution to obtain conductive nanoparticles with enhanced thermal stability, processability, and conductivity. Ngamna *et al.* (2002) utilized the micellar emulsion polymerization method to develop an inkjet-printable nanoformulation of polyaniline. They did this by compromising on the amount of DBSA and APS in order to produce a good quality printable ink with high conductivity [46].

Inkjet-printed polyaniline sensors have a wide application window. The most well known is ammonia. Ammonia has been determined in both gas and liquid forms in various environments. Inkjet-printed polyaniline nanoparticles were used to develop a breath ammonia-monitoring system known as AmBeR[®] [47]. The AmBeR[®] technology quantifies ammonia across the clinically relevant range of 40–2175 parts-per-billion (ppbv) through electrochemical impedance spectroscopy by recording conduction changes of the polyaniline film upon exposure to ammonia concentrations. The quantification of aqueous ammonia leaks in secondary refrigerant systems was also developed [48]. Similarly, this system utilizes impedimetric measurement of ammonia but includes a gas permeable membrane allowing for gaseous ammonia measurements to be conducted in an aqueous environment over the range of 0–100 ppm from +4 to –15 °C in water and brine. Amperometric determination of aqueous ammonia based on inkjet-printed polyaniline nanoparticles modified screen-printed carbon electrodes has also been fabricated. These sensors had 5% reproducibility across the ranges of 0–80 μ M and 0.25–10 mM (Figure 15.3) [49].

Polyaniline is often combined with other materials to form conductive composites with higher selectivity and conductivity. Polyaniline–polystyrene sulfonate (PSS) nanoparticles have been prepared by adjusting the ratio of aniline, PSS,

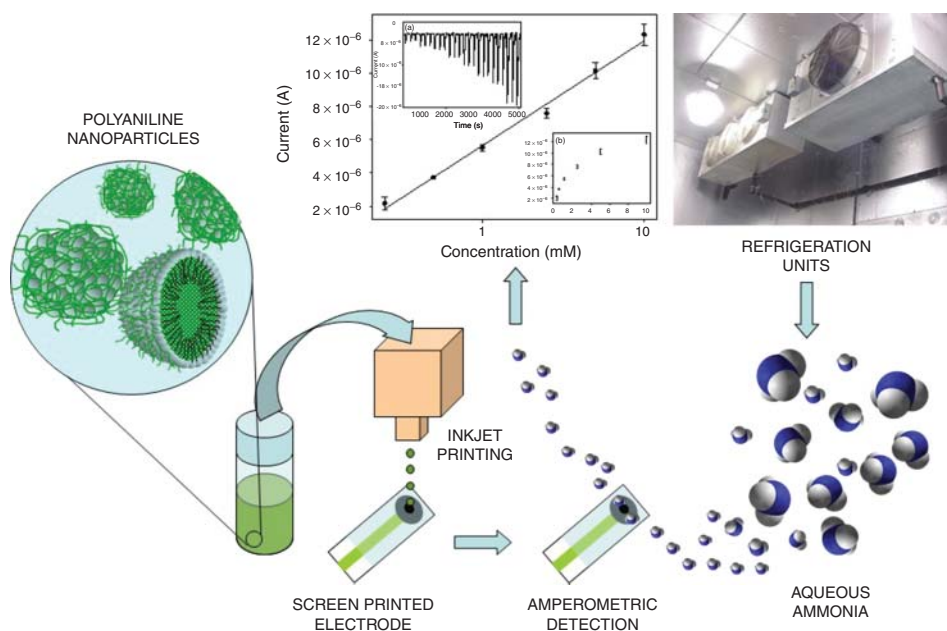


Figure 15.3 Schematic of the inkjet modification process of the interdigitated silver electrode with polyaniline nanoparticles. These sensors lead to excellent correlation between ammonia (0.25–5 mM) and amperometric response. (Crowley *et al.* (2008) [49]. Reproduced with permission of Royal Society of Chemistry.)

and hydrochloric acid. These nanoparticles were then inkjet-printed on paper and were used for ammonia sensing. They displayed reproducible and reversible responses across the ppb scale [50].

Polyaniline-copper chloride (CuCl_2) nanocomposites have been electropolymerized for the determination of hydrogen sulfide (H_2S) [51, 52]. Polyaniline– CuCl_2 solutions have been inkjet-deposited to form a chemiresistor sensor for H_2S determination. CuCl_2 was employed to ensure a shift from the emeraldine salt form to the emeraldine base. Upon exposure to H_2S , the copper bound to the sulfide released HCl , which protonated the emeraldine base back to emeraldine salt, causing an increase in conductivity (Figure 15.4) [54].

A printed device for the determination of urea in serum has been developed by modified screen-printed electrodes using inkjet-printed polyaniline and urease across the range of 2–12 mM ($r^2 = 0.98$) [55]. Polyaniline–gold composites have been synthesized using gold salt as an oxidant to induce chemical oxidative polymerization along with the reduction of HAuCl_4 in solution. This material was then demonstrated as inkjet-printable material, which resulted in high-quality films. This platform may be used for biosensing applications in which a biomolecule is attached to the gold surface [56].

15.3.2 Polypyrrole

Inkjet-printable formation of polypyrrole nanoparticles was developed and combined with enzymes such as HRP and GO. This bioink was inkjet deposited

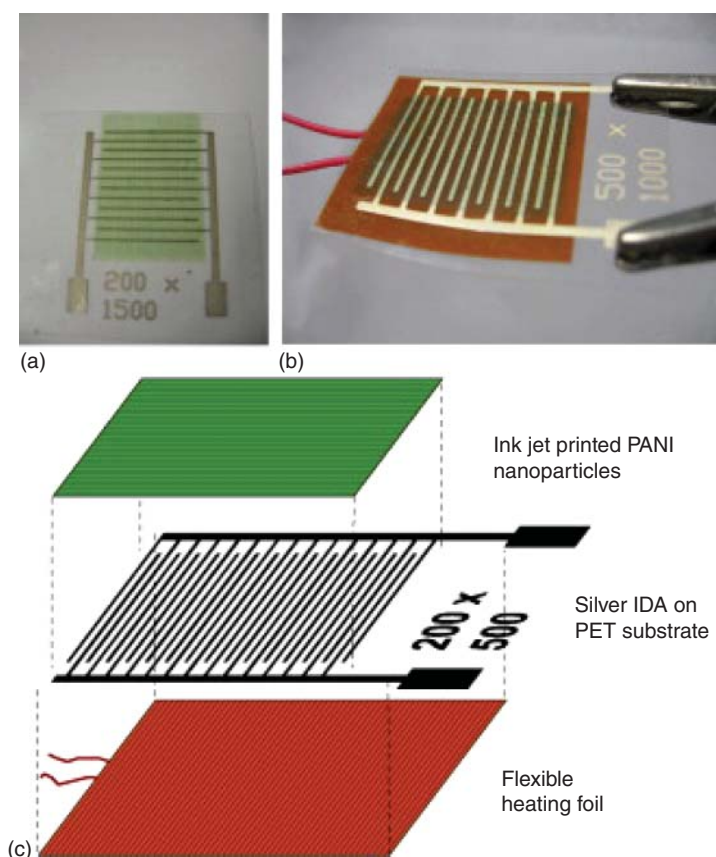


Figure 15.4 Printed polyaniline films for polyethylene terephthalate (PET)-based silver interdigitated electrodes used for gaseous ammonia sensing shown alone (a) and with a thermofoil heater (b). Schematic diagram of polyaniline-modified interdigitated electrode showing different layers of the sensor (c). (Crowley *et al.* (2008) [53]. Reproduced with permission of Elsevier.)

onto screen-printed carbon electrodes. Voltammetric and amperometric measurements were then carried out to determine hydrogen peroxide (H_2O_2) and glucose levels across the linear ranges of $10\text{ }\mu\text{M}$ – 10 mM and 1 – 5 mM , respectively [57].

15.3.3 Prussian Blue

A combination of screen-printed carbon electrodes modified with inkjet-printed Prussian blue nanoparticles for the determination of cholesterol has been reported over the range of 1 – 15 mM ($r^2 = 0.97$) [58]. Prussian blue nanoparticles were synthesized by mixing equimolar amounts of potassium ferrocyanide and iron(III) chloride in the presence of KCl in acidic conditions [59].

15.3.4 PEDOT

Poly(3,4-ethylenedioxythiophene) (PEDOT) is prepared by standard oxidative chemical or electrochemical polymerization methods. It is highly conductive ($400\text{--}600\text{ S cm}^{-1}$), highly transparent, electrochemically stable, and thermally stable (230°C) in thin oxidized films (doped with PF_6^- , BF_6^- , CF_3SO_3) [60]. The processability of PEDOT for inkjet printing applications is very poor as it is an insoluble polymer. However, this has been mitigated by polymerizing it with polystyrene sulfonate (PSS), which is a water polyelectrolyte. This forms a dark blue, water soluble, electrochemically stable, *p*-doped ink. It is moderately transparent and has high electrical conductivity ($1\text{--}10\text{ S cm}^{-1}$) [61].

PEDOT-PSS was first inkjet-printed along with GO for the development of a prototype glucose amperometric biosensor [62]. The preliminary response of the sensor was measured in an aqueous glucose solution in the presence of ferrocene methanol (FeMeOH) as a mediator and resulted in a linear response up to 60 mM in glucose. Although that was not a nanoparticle ink, it did lead onto inkjet print sensor applications typically in combination with nanoparticles as a composite. For example, an enzymatic amperometric sensor was developed for triglyceride detection. Gold nanoparticles and PEDOT-PSS was inkjet-printed onto screen-printed carbon electrodes and operated over a range of $0\text{--}531\text{ mg dl}^{-1}$ [63]. PEDOT-PSS has also been combined with graphene, which was inkjet-printed onto carbon screen-printed electrodes for the amperometric determination of H_2O_2 , nicotinamide adenine dinucleotide (NADH), ferrocyanide, and salbutamol [64, 65]. Aqueous dispersions of PEDOT-PSS [50] have also been inkjet-printed for use as ammonia sensors. Ammonia concentrations between 0.01 and 1000 ppm have been determined.

Although PEDOT-PSS is not as conductive as ITO, it may be possible to replace in some areas such as sensor fabrication, where transparency is not as important as processability [60].

15.4 Carbon Nanomaterials

Carbon is found in two allotropes, diamond and graphite. Diamond has a sp^3 -hybridized carbon structure. Graphite is a sp^2 -hybridized structure and consists of stacked carbon atoms via van der Waals interactions. Carbon fullerenes have been synthesized into tubular carbon networks of single-, double-, or multiwall orientation. Single-walled CNTs (SWCNTs) are single shells of graphene with diameters ranging from 0.4 to 4 nm . They can be rolled up in multiple ways, leading to some having semiconducting properties and others having metallic properties. Multiwalled CNTs (MWCNTs) are composed of multiple shells of graphene and can have diameters ranging from several to tens of nanometers. MWCNTs always have metallic properties due to the direction they get rolled up [3].

15.4.1 Graphene Oxide

Recent years have witnessed many breakthroughs and excitement in graphene research, which have resulted in huge mass production of commercial inks and

sensors [66]. This one-atom thick sheet of carbon combines mechanical strength, high electronic, high surface area, and thermal conductivities. It is impermeable to gases and easily functionalized, making it an attractive option for sensing.

Currently, there are numerous ways to prepare graphene in various orientation, dimensions, and quality. Those that are scalable have been reviewed [67]; they include liquid phase and thermal exfoliation, chemical vapor deposition (CVD), and synthesis on silicon carbide among others. In order for graphene to be inkjet-printed, liquid-phase exfoliation methods have been used to produce colloidal suspensions of graphene following the Hummers' method [68]. Graphite oxide is generated through the addition of potassium permanganate to a solution of graphite, sodium nitrate, and sulfuric acid. This disrupts the sp^2 network and introduces carboxyl or carbonate groups, generating graphene oxide sheets [69]. Sonication, stirring, and centrifugation may then be used to split the graphene sheets into individual platelets. However, this process is problematic because graphene layers tend to aggregate and restack due to van der Waals interactions. 1,5-Dimethyl-pyrrolidone (DMP) and NMP are common solvents used to disperse graphene. However, they are of extremely low viscosity (<2 cP) and often cause dripping from the cartridge nozzles. Concentrations of graphene in these solvents are usually low (<0.1 mg ml^{-1}), so numerous layers are required for optimum performance [4]. DMP and NMP are toxic and cannot be used on a large scale. Surfactants are then added to ensure homogenous dispersion and ideal viscosity.

Functionalization of the graphene surface is often carried out to prevent van der Waals forces. This can be done either by covalent or noncovalent bonding. An example of noncovalent functionalization is the use of pyrene derivatives to stabilize single- and few-layer graphene flakes in aqueous dispersions [70]. Li *et al.* have also developed a simple technology for the deposition of a few layers of graphene using solvent exchange and polymer stabilization, which result in high concentration dispersion. The resulting conductive films had a sheet resistance of ~ 200 k Ω and transmittance of 90% [4].

Inkjet printing of graphene has been demonstrated in the literature [4, 71, 72]. This has been extended to sensor applications [73–75]. Graphene has been inkjet-printed to produce gas detectors, which are extremely sensitive. However, their use is not competitive in the field of gas sensing, which is dominated by metal oxides. This is mainly due to low selectivity and humidity issues. Vapor sensors have been fabricated using films of graphene oxide, and reduced graphene oxides have been inkjet-printed onto a flexible plastic substrate. Vapors in the 100 ppm–500 ppb concentration range were detected in an air sample [73].

Functionalization of graphene has propelled its application into the biosensing arena. Sensors have been fabricated for glucose, cholesterol, hemoglobin, and deoxyribonucleic acid (DNA) [76]. Bioassays have been developed using inkjet-printed graphene oxide nanosheets. Graphene nanosheets emit a stable fluorescence in soluble and dry states and can adsorb various functionalized silver nanoparticles by nonspecific interactions at the surface, which switch off the fluorescence. Silver nanoparticles are dissociated from the nanosheets

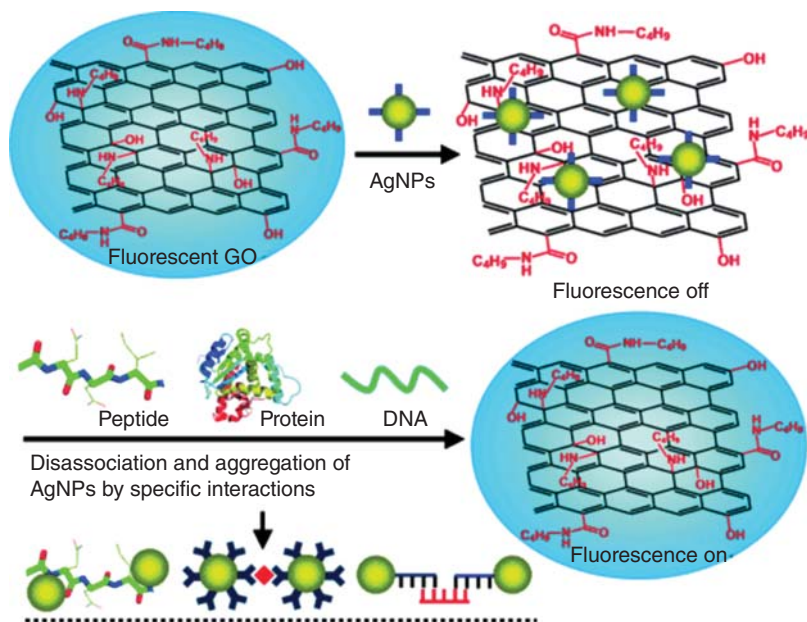


Figure 15.5 The photoluminescent GO nanosheets adsorb functionalized silver nanoparticles leading to quenching of GO fluorescence. The addition of analyte species leads to the dissociation and aggregation of the silver nanoparticles and the fluorescence is recovered. (Mei and Zhang (2012) [77]. Reproduced with permission of Wiley.)

through specific interactions of peptides, protein, or DNA, which turns on the fluorescence (Figure 15.5) [77].

Graphene multianalysis sensing has been forecast for measurements such as gas, pressure, magnetic field, temperature, and strain [67].

15.4.2 Carbon Nanotubes

Carbon nanotubes have become a popular sensing material for many applications due to their rich electrical properties [78]. The earliest records of carbon nanotube (CNT) inkjet printing were reported more than 10 years ago. There are numerous reports in the literature that utilize inkjet-printed CNTs for sensing applications. This is because they consist entirely of surface atoms, which are sensitive to changes in the environment. They can be probed for different electrochemical behaviors by altering the processing steps such as synthesis, cleaning, impurities, storage conditions, and age of the materials [79]. SWCNTs were first used as sensing element for the determination of NH_3 (electron donor) and NO_2 (electron acceptor) based on charge transduction [80]. Since then there has been continued reports of broad uses for CNTs, for example, DNA-hybridization, protein-binding, antibody-antigen and aptamers [81–83], vapors [84], CO_2 [85], dimethyl methylphosphonate (DMMP) [86], trinitrotoluene (TNT) [87], CO [88], H [89–91], and glucose [92].

Fabrication options for CNTs and the potential applications have been covered in an extensive review [93]. CNTs are typically grown using CVD, but other

production methods such as arc discharge and laser ablation are available. The properties of CNT synthesis are detailed in a review found elsewhere [94]. There are many issues surrounding the production of CNT-based inkjet-printable dispersion. CNTs tend to stick together due to van der Waals forces, which have a huge impact, affecting their dispersivity, which results in agglomeration, sedimentation, and inkjet printer cartridge nozzle clogging [95]. It also affects the conductivity of the deposited films as current flows on the surface of the CNTs and cannot reach the inside of the agglomerates. There have been efforts to overcome this, such as dispersion in organic solvents or water using polymers and surfactants and also functionalization of the CNTs. Organic solvents are excellent in dispersing CNTs. They work by adsorbing onto the CNT surface by hydrophobic interaction, which acts as a counter to the strong van der Waals forces that exist between CNTs. However, they need to be removed (usually by rinsing with water) subsequent to printing because they will reduce the conductivity of the films. Typical organic solvents used for printing CNTs are dimethylformamide (DMF) and NMP. Due to their low surface tension, a wetting agent is needed. However, they do have a reported concentration limit of 0.1 mg ml^{-1} when combined with CNT [96]. They are volatile and corrosive and require safe handling. CNTs tend to agglomerate as hydrophobic materials in water. Surfactants and polymers can be used to counter the strong van der Waals forces that exist when CNTs are in water. Surfactants are amphiphilic molecules so they adsorb onto the surface of the CNTs via their hydrophobic tail. This aids dispersion stability via repulsion of the hydrophilic surfactant heads in water allowing the CNTs to be close proximity to each other without bonding. Polymers act in a similar way by wrapping around the CNTs in a helical manner forming a chemical and physical barrier to the van der Waals forces. These processes usually defect the CNTs, resulting in decreased conductivity. A cost-effective and scalable deposition method for generating conductive MWCNTs on paper and polymer surfaces has been presented. MWCNTs were grown by CVD and were carboxylated and dispersed in water to produce an inkjet-printable ink with a sheet resistivity of $\sim 40 \text{ k}\Omega$ [97]. Sodium dodecyl sulfate (SDS) is a surfactant, and it has been employed to reduce van der Waals forces among CNTs. The addition of SDS reduces the viscosity and surface tension causing ink dripping from the printer cartridge nozzles. To provide a satisfactory degree of viscosity, 10–20% ethylene glycol was added. CNTs have been widely employed to sense gases and vapors. SWCNTs are mixed with SDS and disperse readily in water for inkjet printing for alcohol vapor detection [98].

CNT gas-based sensors have been very successful. They have been fabricated by deposition on gold electrodes for gas and organic vapor detection typically with drop casting [99] with detection levels as low as 100 ppm [100]. However, printing carbon nanotubes gives better control over film formation and, therefore, improves the conductivity of the film [95]. Numerous inkjet printing reports of carbon nanotubes have been published since it was first demonstrated [97]. One example is an inkjet-printed alcohol conductivity vapor sensor [101]. This sensor was capable of sensing over the range of $5\text{--}55 \times 10^3 \text{ ppm}$ ($r^2 = 0.9956$). Patterns were seen to have a sheet resistivity of $100 \text{ k}\Omega$ with an optical transparency of 85% [101]. CNT ammonia sensing has been reported by flexible heated



Figure 15.6 Printed films of gellan gum and carbon nanotube–gellan gum composite films. Photograph of flexible transparent composite film printed onto PET. (Panhuis *et al.* (2007) [103]. Reproduced with permission of Royal Society of Chemistry.)

sensors fabricated by inkjet print deposition of a silver array coated with carbon nanofibers decorated with metallic nanoparticles [102]. SW and MWCNTs and biopolymers (gellan and xanthan gum) were combined and inkjet-printed to produce transparent humidity sensors (Figure 15.6) [103].

Light sensors have also been fabricated using inkjet-printed CNTs. MWCNTs have been inkjet-printed onto silver inkjet-printed electrodes to produce infrared sensors onto flexible polyamide substrate. Infrared sensitivities were as high as 1.2 kV W^{-1} [104]. In another example, CNTs were combined with cadmium telluride (CdTe) nanocrystals to produce an inkjet-printed light sensor [105]. The authors also present a similar device based on inkjet-printed MWCNTs onto a transparent flexible substrate with inkjet-printed silver contacts (Figure 15.7). This device was used to absorb light in both directions of the substrate while transmitting energy. Both devices are operated at room temperature, are low cost to fabricate, and are easily scalable.

CNTs have been used to determine antioxidants in biological systems. An all-printed sensor has been fabricated by inkjet printing carbon active layer made of SWCNT inkjet-printed onto silver nanoparticle connection layer. The voltammetric determination of antioxidant power of ascorbic acid solutions and biological samples such as erythrocyte concentrations from blood donors was measured [106]. Monitoring of antioxidant in blood and saliva may provide relevant information about the status of the antioxidant system and the overall health status of a person.

A paper-based inkjet-printed electrochemical sensor consisting of CNT working, counter, and reference electrodes has been reported for the voltammetric measurement of iron ion and dopamine (Figure 15.8) with linear ranges of $10\text{--}200 \text{ }\mu\text{M}$ ($r^2 = 0.9909$) and $10\text{--}100 \text{ }\mu\text{M}$ ($r^2 = 0.9937$), respectively [107].

An inkjet-printed Nafion–MWCNT sensor was developed for rapid dopamine determination in undiluted human serum. This platform successfully demonstrated direct detection of dopamine concentrations over the range



Figure 15.7 Fabricated MWCNT-NP's inkjet-printed sensor on a flexible transparent substrate. The MWCNT channel is printed between printed silver electrodes. The substrate is polyethylene terephthalate (PET). Similar devices showed response at the same range and spectra; however, the noise was doubled. (Katzir *et al.* (2014) [105]. Reproduced with permission of Elsevier.)

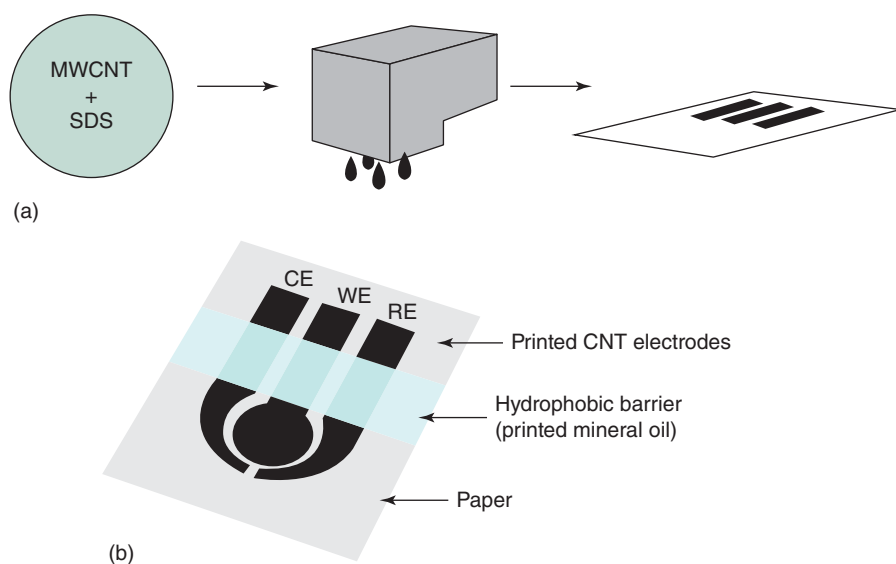


Figure 15.8 Illustration of the fabrication process: (a) mixing of carbon nanotube ink by using optimal MWCNT–SDS ratio in deionized water, followed by inkjet printing the carbon nanotube ink and (b) the sensor composed of counter, working, and reference electrodes, with a hydrophobic barrier on top [107]. (da Costa *et al.* (2015) <http://jss.ecsdl.org/content/4/10/S3044.short>.)

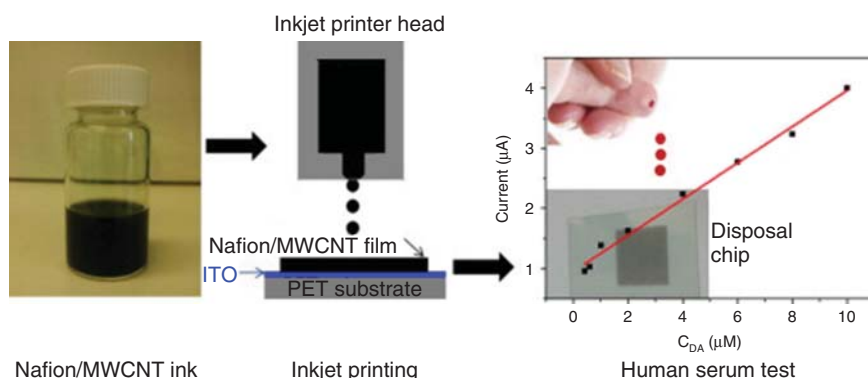


Figure 15.9 Schematic of the inkjet modification process of the Nafion–MWCNT sensor. These sensors lead to an excellent correlation between dopamine (0.1–10 μM) and amperometric response. (Zhao *et al.* (2013) [108]. Reproduced with permission of Elsevier.)

of 0.1–10 μM ($r^2 = 0.999$) using voltammetric and amperometric methods (Figure 15.9) [108].

Inkjet printing of graphene and CNTs has become so popular that dispersions are available commercially for the purpose of inkjet printing for the fabrication of electrodes with high electrical conductivity and electrochemical activity. They are also available as functionalized materials by the manufacturer. However, carbon is not yet competitive with traditional metallic, which have higher conductivities. In order to achieve acceptable conductivities, hundreds of inkjet print layers are still required.

15.5 Future Outlooks and Conclusions

As modern sensing applications move toward decentralization, the demand for integrated sensors is ever increasing. The next generation of printed sensor will definitely involve multianalyte determinations, flexibility, and miniaturization using integrated printed devices. Ideally, a fully printed device should be integrated into a system that consists of the sensing device, display, battery, measurement chip, communications chip, and a push button [109]. This device should have the capacity to be interfaced with a miniaturized potentiostat. Miniaturized potentiostats are being developed in parallel with sensor technologies to produce truly localized testing. Inkjet printing may be combined with other commercial printing techniques such as roll-to-roll screen printing to produce fully integrated devices. Multianalyte sensing is also an option for printed sensors where arrays can be easily fabricated and designed for individual assays from the one sample.

References

- 1 Choi, H.W., Zhou, T., Singh, M., and Jabbour, G.E. (2015) Recent developments and directions in printed nanomaterials. *Nanoscale*, 7 (8), 3338–3355.

- 2 Gonzalez-Macia, L., Morrin, A., Smyth, M.R., and Killard, A.J. (2010) Advanced printing and deposition methodologies for the fabrication of biosensors and biodevices. *Analyst*, **135** (5), 845–867.
- 3 Cummins, G. and Desmulliez, M.P.Y. (2012) Inkjet printing of conductive materials: A review. *Circuit World*, **38** (4), 193–213.
- 4 Li, J., Ye, F., Vaziri, S., Muhammed, M., Lemme, M.C., and Ostling, M. (2013) Efficient inkjet printing of graphene. *Adv. Mater.*, **25** (29), 3985–3992.
- 5 Magdassi, S. (2010) *The Chemistry of Inkjet Inks*, World Scientific, Singapore.
- 6 Fuller, S.B., Wilhelm, E.J., and Jacobson, J.M. (2002) Ink-jet printed nanoparticle microelectromechanical systems. *J. Microelectromech. Syst.*, **11** (1), 54–60.
- 7 Zhao, N., Chiesa, M., Sirringhaus, H., Li, Y., and Wu, Y. (2007) Self-aligned inkjet printing of highly conducting gold electrodes with submicron resolution. *J. Appl. Phys.*, **101** (6), 064513.
- 8 Chow, E., Herrmann, J., Barton, C.S., Raguse, B., and Wieczorek, L. (2009) Inkjet-printed gold nanoparticle chemiresistors: Influence of film morphology and ionic strength on the detection of organics dissolved in aqueous solution. *Anal. Chim. Acta*, **632** (1), 135–142.
- 9 Jensen, G.C., Krause, C.E., Sotzing, G.A., and Rusling, J.F. (2011) Inkjet-printed gold nanoparticle electrochemical arrays on plastic. Application to immunodetection of a cancer biomarker protein. *Phys. Chem. Chem. Phys.*, **13** (11), 4888–4894.
- 10 Deng, M., Zhang, X., Zhang, Z., Xin, Z., and Song, Y. (2014) A gold nanoparticle ink suitable for the fabrication of electrochemical electrode by inkjet printing. *J. Nanosci. Nanotechnol.*, **14** (7), 5114–5119.
- 11 Krause, C.E., Otieno, B.A., Latus, A., Faria, R.C., Patel, V., Gutkind, J.S., and Rusling, J.F. (2013) Rapid microfluidic immunoassays of cancer biomarker proteins using disposable inkjet-printed gold nanoparticle arrays. *Chemistry-Open*, **2** (4), 141–145.
- 12 Marsico, A.L.M., Czeran, B., Duncan, B., Elci, S.G., Jiang, Y., Onasch, T.B., Wormhoudt, J., Rotello, V.M., and Vachet, R.W. (2015) Inkjet-printed gold nanoparticle surfaces for the detection of low molecular weight biomolecules by laser desorption/ionization mass spectrometry. *J. Am. Soc. Mass. Spectrom.*, **26** (11), 1931–1937.
- 13 Lee, S.H., Shin, K.Y., Hwang, J.Y., Kang, K.T., and Kang, H.S. (2008) Silver inkjet printing with control of surface energy and substrate temperature. *J. Micromech. Microeng.*, **18** (7), 075014.
- 14 Kim, D. and Moon, J. (2005) Highly conductive ink jet printed films of nanosilver particles for printable electronics. *Electrochem. Solid-State Lett.*, **8** (11), J30–J33.
- 15 Chiolerio, A., Maccioni, G., Martino, P., Cotto, M., Pandolfi, P., Rivolo, P., Ferrero, S., and Scaltrito, L. (2011) Inkjet printing and low power laser annealing of silver nanoparticle traces for the realization of low resistivity lines for flexible electronics. *Microelectron. Eng.*, **88** (8), 2481–2483.
- 16 Vaseem, M., Lee, K.M., Hong, A., and Hahn, Y. (2012) Inkjet printed fractal-connected electrodes with silver nanoparticle ink. *ACS Appl. Mater. Interfaces*, **4** (6), 3300–3307.

- 17 Nge, T.T., Nogi, M., and Suganuma, K. (2013) Electrical functionality of inkjet-printed silver nanoparticle conductive tracks on nanostructured paper compared with those on plastic substrates. *J. Mater. Chem. C*, **1** (34), 5235–5243.
- 18 Wang, J., Yang, L., Liu, B., Jiang, H., Liu, R., Yang, J., Han, G., Mei, Q., and Zhang, Z. (2014) Inkjet-printed silver nanoparticle paper detects airborne species from crystalline explosives and their ultratrace residues in open environment. *Anal. Chem.*, **86** (7), 3338–3345.
- 19 Andersson, H., Manuilskiy, A., Unander, T., Lidenmark, C., Forsberg, S., and Nilsson, H. (2012) Inkjet printed silver nanoparticle humidity sensor with memory effect on paper. *IEEE Sens. J.*, **12** (6), 1901–1905.
- 20 Rozenberg, G.G., Bresler, E., Speakman, S.P., Jeynes, C., and Steinke, J.H.G. (2002) Patterned low temperature copper-rich deposits using inkjet printing. *Appl. Phys. Lett.*, **81** (27), 5249–5251.
- 21 Petukhov, D.I., Kirikova, M.N., Bessonov, A.A., and Bailey, M.J.A. (2014) Nickel and copper conductive patterns fabricated by reactive inkjet printing combined with electroless plating. *Mater. Lett.*, **132**, 302–306.
- 22 Li, D., Sutton, D., Burgess, A., Graham, D., and Calvert, P.D. (2009) Conductive copper and nickel lines via reactive inkjet printing. *J. Mater. Chem.*, **19** (22), 3719–3724.
- 23 Niittynen, J., Sowade, E., Kang, H., Baumann, R.R., and Mantysalo, M. (2015) Comparison of laser and intense pulsed light sintering (IPL) for inkjet-printed copper nanoparticle layers. *Sci. Rep.*, **5**, 8832.
- 24 Kang, J.S., Kim, H.S., Ryu, J., Hahn, H.T., Jang, S., and Joung, J.W. (2010) Inkjet printed electronics using copper nanoparticle ink. *J. Mater. Sci.: Mater. Electron.*, **21** (11), 1213–1220.
- 25 Ishida, Y., Nakagawa, G., and Asano, T. (2007) Inkjet printing of nickel nano-sized particles for metal-induced crystallization of amorphous silicon. *Jpn. J. Appl. Phys., Part 1*, **46** (9B), 6437–6443.
- 26 Jang, H.W., Kim, J., Kim, H., Yoon, Y., Lee, S., Hwang, H., and Kim, J. (2010) Fabrication of nonsintered alumina-resin hybrid films by inkjet-printing technology. *Jpn. J. Appl. Phys.*, **49** (7), 071501.
- 27 Mogalicherla, A.K., Lee, S., Pfeifer, P., and Dittmeyer, R. (2014) Drop-on-demand inkjet printing of alumina nanoparticles in rectangular microchannels. *Microfluid. Nanofluid.*, **16** (4), 655–666.
- 28 Hwang, M., Kim, J., Kim, H., Yoon, Y., Hyun, S., Kim, J., Lee, S., and Moon, J. (2010) Inkjet-printing of nonsintered alumina-resin hybrid films and their dielectric properties. *J. Appl. Phys.*, **108** (10), 102809.
- 29 Singh, M., Haverinen, H.M., Dhagat, P., and Jabbour, G.E. (2010) Inkjet printing-process and its applications. *Adv. Mater.*, **22** (6), 673–685.
- 30 Banica, F.G. (2012) *Chemical Sensors and Biosensors*, John Wiley & Sons. Ltd., West Sussex, UK.
- 31 Ihalainen, P., Majumdar, H., Viitala, T., Tornngren, B., Narjeoja, T., Maattanen, A., Sarfraz, J., Harma, H., Yliperttula, M., Osterbacka, R., and Peltonen, J. (2013) Application of paper-supported printed gold electrodes for impedimetric immunosensor development. *Biosensors*, **3** (1), 1–17.

- 32 Maattanen, A., Vanamo, U., Ihalainen, P., Pulkkinen, P., Tenhu, H., Bobacka, J., and Peltonen, J. (2013) A low-cost paper-based inkjet-printed platform for electrochemical analyses. *Sens. Actuators, B*, **177**, 153–162.
- 33 Hu, C., Bai, X., Wang, Y., Jin, W., Zhang, X., and Hu, S. (2012) Inkjet printing of nanoporous gold electrode arrays on cellulose membranes for high-sensitive paper-like electrochemical oxygen sensors using ionic liquid electrolytes. *Anal. Chem.*, **84** (8), 3745–3750.
- 34 Magdassi, S., Grouchko, M., Berezin, O., and Kamyshny, A. (2010) Triggering the sintering of silver nanoparticles at room temperature. *ACS Nano*, **4** (4), 1943–1948.
- 35 Molina-Lopez, F., Briand, D., and de Rooij, N.F. (2012) All additive inkjet printed humidity sensors on plastic substrate. *Sens. Actuators, B*, **166**, 212–222.
- 36 Magdassi, S., Grouchko, M., and Kamyshny, A. (2010) Copper nanoparticles for printed electronics: Routes towards achieving oxidation stability. *Materials*, **3** (9), 4626–4638.
- 37 Grouchko, M., Kamyshny, A., Ben-Ami, K., and Magdassi, S. (2009) Synthesis of copper nanoparticles catalyzed by pre-formed silver nanoparticles. *J. Nanopart. Res.*, **11** (3), 713–716.
- 38 Zhang, Y., Zhu, P., Li, G., Zhao, T., Fu, X., Sun, R., Zhou, F., and Wong, C. (2014) Facile preparation of monodisperse, impurity-free, and antioxidation copper nanoparticles on a large scale for application in conductive Ink. *ACS Appl. Mater. Interfaces*, **6** (1), 560–567.
- 39 Kim, D.S., Khan, A., Rahman, K., Khan, S., Kim, H.C., and Choi, K.H. (2011) Drop-on-demand direct printing of colloidal copper nanoparticles by electrohydrodynamic atomization. *Mater. Manuf. Processes*, **26** (9), 1196–1201.
- 40 Kukkola, J., Mohl, M., Leino, A., Toth, G., Wu, M., Shchukarev, A., Popov, A., Mikkola, J., Lauri, J., Riihimäki, M., Lappalainen, J., Jantunen, H., and Kordas, K. (2012) Inkjet-printed gas sensors: metal decorated WO₃ nanoparticles and their gas sensing properties. *J. Mater. Chem.*, **22** (34), 17878–17886.
- 41 Liu, X., Tarn, T., Huang, F., and Fan, J. (2015) Recent advances in inkjet printing synthesis of functional metal oxides. *Particuology*, **19**, 1–13.
- 42 Niederberger, M. and Pinna, N. (2009) *Metal Oxide Nanoparticles in Organic Solvents*, Springer-Verlag, London.
- 43 Yoon, H. and Jang, J. (2009) Conducting-polymer nanomaterials for high-performance sensor applications: Issues and challenges. *Adv. Funct. Mater.*, **19** (10), 1567–1576.
- 44 Meixner, R.M., Cibis, D., Krueger, K., and Goebel, H. (2008) Characterization of polymer inks for drop-on-demand printing systems. *Microsyst. Technol.*, **14** (8), 1137–1142.
- 45 Han, M.G., Cho, S.K., Oh, S.G., and Im, S.S. (2002) Preparation and characterization of polyaniline nanoparticles synthesized from DBSA micellar solution. *Synth. Met.*, **126** (1), 53–60.
- 46 Ngamna, O., Morrin, A., Killard, A.J., Moulton, S.E., Smyth, M.R., and Wallace, G.G. (2007) Inkjet printable polyaniline nanoformulations. *Langmuir*, **23** (16), 8569–8574.

- 47 Hibbard, T., Crowley, K., Kelly, F., Ward, F., Holian, J., Watson, A., and Killard, A.J. (2013) Point of care monitoring of hemodialysis patients with a breath ammonia measurement device based on printed polyaniline nanoparticle sensors. *Anal. Chem.*, **85** (24), 12158–12165.
- 48 Subramanian, R., Crowley, K., Morrin, A., and Killard, A.J. (2013) A sensor probe for the continuous in situ monitoring of ammonia leakage in secondary refrigerant systems. *Anal. Methods*, **5** (1), 134–140.
- 49 Crowley, K., O'Malley, E., Morrin, A., Smyth, M.R., and Killard, A.J. (2008) An aqueous ammonia sensor based on an inkjet-printed polyaniline nanoparticle-modified electrode. *Analyst*, **133** (3), 391–399.
- 50 Jang, J., Ha, J., and Cho, J. (2007) Fabrication of water-dispersible polyaniline-poly(4-styrenesulfonate) nanoparticles for inkjet-printed chemical-sensor applications. *Adv. Mater.*, **19** (13), 1772–1775.
- 51 Shirsat, M.D., Bangar, M.A., Deshusses, M.A., Myung, N.V., and Mulchandani, A. (2009) Polyaniline nanowires-gold nanoparticles hybrid network based chemiresistive hydrogen sulfide sensor. *Appl. Phys. Lett.*, **94** (8), 083502.
- 52 Virji, S., Huang, J., Kaner, R., and Weiller, B. (2004) Polyaniline nanofiber gas sensors: Examination of response mechanisms. *Nano Lett.*, **4** (3), 491–496.
- 53 Crowley, K., Morrin, A., Hernandez, A., O'Malley, E., Whitten, P.G., Wallace, G.G., Smyth, M.R., and Killard, A.J. (2008) Fabrication of an ammonia gas sensor using inkjet-printed polyaniline nanoparticles. *Talanta*, **77** (2), 710–717.
- 54 Crowley, K., Smyth, M.R., Killard, A.J., and Morrin, A. (2013) Printing polyaniline for sensor applications. *Chem. Pap.*, **67** (8), 771–780.
- 55 Suman, O'Reilly, E., Kelly, M., Morrin, A., Smyth, M.R., and Killard, A.J. (2011) Chronocoulometric determination of urea in human serum using an inkjet printed biosensor. *Anal. Chim. Acta*, **697** (1–2), 98–102.
- 56 Lenhart, N., Crowley, K., Killard, A.J., Smyth, M.R., and Morrin, A. (2011) Inkjet printable polyaniline-gold dispersions. *Thin Solid Films*, **519** (13), 4351–4356.
- 57 Weng, B., Morrin, A., Shepherd, R., Crowley, K., Killard, A.J., Innis, P.C., and Wallace, G.G. (2014) Wholly printed polypyrrole nanoparticle-based biosensors on flexible substrate. *J. Mater. Chem. B*, **2** (7), 793–799.
- 58 Cinti, S., Arduini, F., Moscone, D., Palleschi, G., Gonzalez-Macia, L., and Killard, A.J. (2015) Cholesterol biosensor based on inkjet-printed Prussian blue nanoparticle-modified screen-printed electrodes. *Sens. Actuators, B*, **221**, 187–190.
- 59 Chen, J., Miao, Y., and Wu, X. (2007) Immobilization of Prussian blue nanoparticles onto thiol SAM modified Au electrodes for analysis of DL-homocysteine. *Colloid J.*, **69** (5), 660–665.
- 60 Yoshioka, Y. and Jabbour, G.E. (2006) Desktop inkjet printer as a tool to print conducting polymers. *Synth. Met.*, **156** (11–13), 779–783.
- 61 Aleshin, A.N., Williams, S.R., and Heeger, A.J. (1998) Transport properties of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate). *Synth. Met.*, **94** (2), 173–177.

- 62 Setti, L., Fraleoni-Morgera, A., Ballarin, B., Filippini, A., Frascaro, D., and Piana, C. (2005) An amperometric glucose biosensor prototype fabricated by thermal inkjet printing. *Biosens. Bioelectron.*, **20** (10), 2019–2026.
- 63 Phongphut, A., Sriprachuabwong, C., Wisitsoraat, A., Tuantranont, A., Prichanont, S., and Sritongkham, P. (2013) A disposable amperometric biosensor based on inkjet-printed Au/PEDOT-PSS nanocomposite for triglyceride determination. *Sens. Actuators, B*, **178**, 501–507.
- 64 Sriprachuabwong, C., Karuwan, C., Wisitsorratt, A., Phokharatkul, D., Lomas, T., Sritongkham, P., and Tuantranont, A. (2012) Inkjet-printed graphene-PEDOT:PSS modified screen printed carbon electrode for biochemical sensing. *J. Mater. Chem.*, **22** (12), 5478–5485.
- 65 Karuwan, C., Sriprachuabwong, C., Wisitsoraat, A., Phokharatkul, D., Sritongkham, P., and Tuantranont, A. (2012) Inkjet-printed graphene-poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) modified on screen printed carbon electrode for electrochemical sensing of salbutamol. *Sens. Actuators, B*, **161** (1), 549–555.
- 66 Geim, A.K. and Novoselov, K.S. (2007) The rise of graphene. *Nat. Mater.*, **6** (3), 183–191.
- 67 Novoselov, K.S., Fal'ko, V.I., Colombo, L., Gellert, P.R., Schwab, M.G., and Kim, K. (2012) A roadmap for graphene. *Nature*, **490** (7419), 192–200.
- 68 Hummers, W.S. and Offeman, R.E. (1958) Preparation of graphitic oxide. *J. Am. Chem. Soc.*, **6**, 1339.
- 69 Torrisi, F., Hasan, T., Wu, W., Sun, Z., Lombardo, A., Kulmala, T.S., Hsieh, G., Jung, S., Bonaccorso, F., Paul, P.J., Chu, D., and Ferrari, A.C. (2012) Inkjet-printed graphene electronics. *ACS Nano*, **6** (4), 2992–3006.
- 70 Parviz, D., Das, S., Ahmed, H.S.T., Irin, F., Bhattacharia, S., and Green, M.J. (2012) Dispersions of non-covalently functionalized graphene with minimal stabilizer. *ACS Nano*, **6** (10), 8857–8867.
- 71 Arapov, K., Abbel, R., de With, G., and Friedrich, H. (2014) Inkjet printing of graphene. *Faraday Discuss.*, **173**, 323–336.
- 72 Shin, K., Hong, J., and Jang, J. (2011) Flexible and transparent graphene films as acoustic actuator electrodes using inkjet printing. *Chem. Commun.*, **47** (30), 8527–8529.
- 73 Dua, V., Surwade, S.P., Ammu, S., Agnihotra, S.R., Jain, S., Roberts, K.E., Park, S., Ruoff, R.S., and Manohar, S.K. (2010) All-organic vapor sensor using inkjet-printed reduced graphene oxide. *Angew. Chem., Int. Ed.*, **49** (12), 2154–2157.
- 74 Huang, L., Huang, Y., Liang, J., Wan, X., and Chen, Y. (2011) Graphene-based conducting inks for direct inkjet printing of flexible conductive patterns and their applications in electric circuits and chemical sensors. *Nano Res.*, **4** (7), 675–684.
- 75 Le, T., Lakafosis, V., Lin, Z., Wong, C.P. and Tentzeris, M.M. (2012) *Inkjet-printed graphene-based wireless gas sensor modules*. 2012 IEEE 62nd Electronic Components and Technology Conference (Ectc), 1003–1008.
- 76 Kuila, T., Bose, S., Khanra, P., Mishra, A.K., Kim, N.H., and Lee, J.H. (2011) Recent advances in graphene-based biosensors. *Biosens. Bioelectron.*, **26** (12), 4637–4648.

- 77 Mei, Q. and Zhang, Z. (2012) Photoluminescent graphene oxide ink to print sensors onto microporous membranes for versatile visualization bioassays. *Angew. Chem., Int. Ed.*, **51** (23), 5602–5606.
- 78 Zhang, T., Mubeen, S., Myung, N.V., and Deshusses, M.A. (2008) Recent progress in carbon nanotube-based gas sensors. *Nanotechnology*, **19** (33), 332001.
- 79 Ambrosi, A. and Pumera, M. (2010) Nanographite impurities dominate electrochemistry of carbon nanotubes. *Chem. - Eur. J.*, **16** (36), 10946–10949.
- 80 Kong, J., Franklin, N.R., Zhou, C.W., Chapline, M.G., Peng, S., Cho, K.J., and Dai, H.J. (2000) Nanotube molecular wires as chemical sensors. *Science*, **287** (5453), 622–625.
- 81 Kim, S.N., Rusling, J.F., and Papadimitrakopoulos, F. (2007) Carbon nanotubes for electronic and electrochemical detection of biomolecules. *Adv. Mater.*, **19** (20), 3214–3228.
- 82 Allen, B.L., Kichambare, P.D., and Star, A. (2007) Carbon nanotube field-effect-transistor-based biosensors. *Adv. Mater.*, **19** (11), 1439–1451.
- 83 Heller, D.A., Jeng, E.S., Yeung, T.K., Martinez, B.M., Moll, A.E., Gastala, J.B., and Strano, M.S. (2006) Optical detection of DNA conformational polymorphism on single-walled carbon nanotubes. *Science*, **311** (5760), 508–511.
- 84 Snow, E.S., Perkins, F.K., and Robinson, J.A. (2006) Chemical vapor detection using single-walled carbon nanotubes. *Chem. Soc. Rev.*, **35** (9), 790–798.
- 85 Star, A., Han, T.R., Joshi, V., Gabriel, J.C.P., and Gruner, G. (2004) Nanoelectronic carbon dioxide sensors. *Adv. Mater.*, **16** (22), 2049–2054.
- 86 Yu, C., Hao, Q., Saha, S., Shi, L., Kong, X.Y., and Wang, Z.L. (2005) Integration of metal oxide nanobelts with microsystems for nerve agent detection. *Appl. Phys. Lett.*, **86** (6), 063101.
- 87 Chen, P., Sukcharoenchoke, S., Ryu, K., de Arco, L.G., Badmaev, A., Wang, C., and Zhou, C. (2010) 2,4,6-Trinitrotoluene (TNT) chemical sensing based on aligned single-walled carbon nanotubes and ZnO nanowires. *Adv. Mater.*, **22** (17), 1900–1904.
- 88 Fu, D., Lim, H., Shi, Y., Dong, X., Mhaisalkar, S.G., Chen, Y., Moochhala, S., and Li, L. (2008) Differentiation of gas molecules using flexible and all-carbon nanotube devices. *J. Phys. Chem. C*, **112** (3), 650–653.
- 89 Kong, J., Chapline, M.G., and Dai, H.J. (2001) Functionalized carbon nanotubes for molecular hydrogen sensors. *Adv. Mater.*, **13** (18), 1384–1386.
- 90 Mubeen, S., Zhang, T., Yoo, B., Deshusses, M.A., and Myung, N.V. (2007) Palladium nanoparticles decorated single-walled carbon nanotube hydrogen sensor. *J. Phys. Chem. C*, **111** (17), 6321–6327.
- 91 Sun, Y. and Wang, H.H. (2007) Electrodeposition of Pd nanoparticles on single-walled carbon nanotubes for flexible hydrogen sensors. *Appl. Phys. Lett.*, **90** (21), 213107.
- 92 Lee, D. and Cui, T. (2010) Low-cost, transparent, and flexible single-walled carbon nanotube nanocomposite based ion-sensitive field-effect transistors for pH/glucose sensing. *Biosens. Bioelectron.*, **25** (10), 2259–2264.

- 93 Park, S., Vosguerichian, M., and Bao, Z. (2013) A review of fabrication and applications of carbon nanotube film-based flexible electronics. *Nanoscale*, **5** (5), 1727–1752.
- 94 Hu, L., Hecht, D.S., and Gruener, G. (2010) Carbon nanotube thin films: Fabrication, properties, and applications. *Chem. Rev.*, **110** (10), 5790–5844.
- 95 Tortorich, R.P. and Choi, J. (2013) Inkjet printing of carbon nanotubes. *Nanomaterials*, **3** (3), 453–468.
- 96 Hecht, D.S., Hu, L., and Irvin, G. (2011) Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Adv. Mater.*, **23** (13), 1482–1513.
- 97 Kordas, K., Mustonen, T., Toth, G., Jantunen, H., Lajunen, M., Soldano, C., Talapatra, S., Kar, S., Vajtai, R., and Ajayan, P.M. (2006) Inkjet printing of electrically conductive patterns of carbon nanotubes. *Small*, **2** (8–9), 1021–1025.
- 98 Mabrook, M.F., Pearson, C., Jombert, A.S., Zeze, D.A., and Petty, M.C. (2009) The morphology, electrical conductivity and vapour sensing ability of inkjet-printed thin films of single-wall carbon nanotubes. *Carbon*, **47** (3), 752–757.
- 99 Li, J., Lu, Y.J., Ye, Q., Cinke, M., Han, J., and Meyyappan, M. (2003) Carbon nanotube sensors for gas and organic vapor detection. *Nano Lett.*, **3** (7), 929–933.
- 100 Chopra, S., McGuire, K., Gothard, N., Rao, A.M., and Pham, A. (2003) Selective gas detection using a carbon nanotube sensor. *Appl. Phys. Lett.*, **83** (11), 2280–2282.
- 101 Small, W.R. and Panhuis, M.i.h. (2007) Inkjet printing of transparent, electrically conducting single-walled carbon-nanotube composites. *Small*, **3** (9), 1500–1503.
- 102 Claramunt, S., Monereo, O., Boix, M., Leghrib, R., Prades, J.D., Cornet, A., Merino, P., Merino, C., and Cirera, A. (2013) Flexible gas sensor array with an embedded heater based on metal decorated carbon nanofibres. *Sens. Actuators, B*, **187**, 401–406.
- 103 Panhuis, M.i.h., Heurtematte, A., Small, W.R., and Paunov, V.N. (2007) Inkjet printed water sensitive transparent films from natural gum-carbon nanotube composites. *Soft Matter*, **3** (7), 840–843.
- 104 Gohier, A., Dhar, A., Gorintin, L., Bondavalli, P., Bonnassieux, Y., and Cojocar, C.S. (2011) All-printed infrared sensor based on multiwalled carbon nanotubes. *Appl. Phys. Lett.*, **98** (6), 063103.
- 105 Katzir, E., Yochelis, S., Paltiel, Y., Azoubel, S., Shimoni, A., and Magdassi, S. (2014) Tunable inkjet printed hybrid carbon nanotubes/nanocrystals light sensor. *Sens. Actuators, B*, **196**, 112–116.
- 106 Lesch, A., Cortes-Salazar, F., Prudent, M., Delobel, J., Rastgar, S., Lion, N., Tissot, J., Tacchini, P., and Girault, H.H. (2014) Large scale inkjet-printing of carbon nanotubes electrodes for antioxidant assays in blood bags. *J. Electroanal. Chem.*, **717**, 61–68.
- 107 da Costa, T.H., Song, E., Tortorich, R.P., and Choi, J. (2015) A paper-based electrochemical sensor using inkjet-printed carbon nanotube electrodes. *ECS J. Solid State Sci. Technol.*, **4** (10), S3044–S3047.

- 108 Zhao, J., Yu, Y., Weng, B., Zhang, W., Harris, A.T., Minett, A.I., Yue, Z., Huang, X., and Chen, J. (2013) Sensitive and selective dopamine determination in human serum with inkjet printed Nafion/MWCNT chips. *Electrochem. Commun.*, **37**, 32–35.
- 109 Beni, V., Nilsson, D., Arven, P., Norberg, P., Gustafsson, G., and Turner, A.P.F. (2015) Printed electrochemical instruments for biosensors. *ECS J. Solid State Sci. Technol.*, **4** (10), S3001–S3005.

16

Electrochromics for Printed Displays and Smart Windows

Pooi See Lee, Guofa Cai, Alice L.-S. Eh, and Peter Darmawan

16.1 Overview on Electrochromics

For the first time, at the COP21 (21st Conference of Parties) also known as the 2015 Paris Climate Conference, a historical moment was made by the signing of a legally binding landmark accord by representatives of 195 nations that aims to lower global warming and greenhouse emissions to prevent drastic climate changes [1, 2]. Given the fact that almost half of the global carbon emissions came from the world's richest 10%, it is to be expected that governments from all over the world will push for green initiatives to cut down fossil fuel consumptions for our energy needs [3]. One of such initiatives that governments of developed nations are pushing for is the green building initiative, whose aim is to advocate green building design, practices, and technologies and drive environmental sustainability in the building and construction industry.

The electrochromic (EC) technology changes its optical state through the intercalation and extraction of small ions when an external electrical field is applied. It consists of several layers that are sandwiched between two transparent electrodes. The change in the optical state of the EC device is a result of reversible switching of chemical species among different redox states with distinct absorption or reflection spectra that is induced by a potential difference or the application of electrical current [4–6]. Many EC materials are available, ranging from organic and inorganic to small molecules. Broadly, EC materials can be categorized into two sections: “cathodic” and “anodic”. For the “cathodic” EC materials, the color change from transparent state to dark state is observed when they are reduced during cathodic polarization process. Thus for “anodic” EC materials, color change from transparent state to dark state is observed when they are oxidized during anodic polarization process.

Electrochromic devices (ECD) typically consist of an electrolyte layer that is sandwiched between an EC active material deposited on a transparent conducting electrode (TCE) and a complementary EC material/ion-storage layer deposited on the other TCE as shown in Figure 16.1.

Tungsten trioxide (WO_3) films was first observed about 35 years ago to exhibit the electrochromic property, and this material has remained today as one of the most promising and well-studied materials for EC devices [7–10]. The method

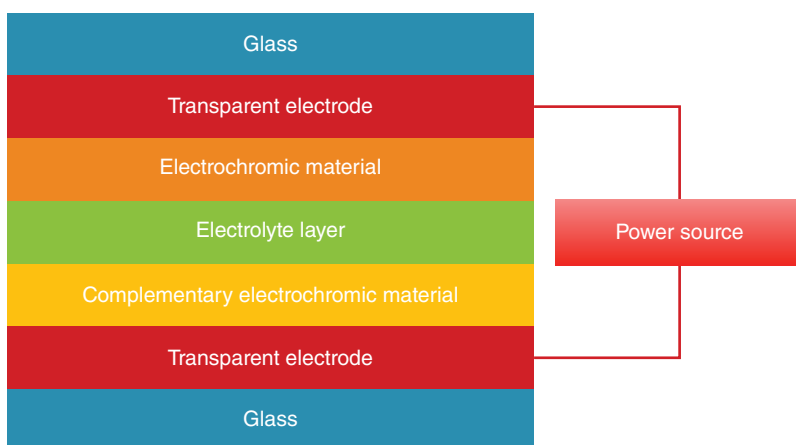


Figure 16.1 Schematic illustration of a typical electrochromic device.

of application/deposition of tungsten oxide films onto the TCE is wide-ranging, which includes, but not limited to, sputtering [11–13], spray pyrolysis [13–15], electrodeposition [13, 16–20], thermal evaporation [13, 21, 22], and, more recently, inkjet printing [23–26]. However, at the time of writing of this chapter, only EC materials deposited by sputtering had been used in the commercial ready devices, thus considered a more mature deposition technique.

ECDs have been deployed in the automotive industry, in particular, as auto-dimming rear view mirrors in luxury cars. Gentex Corporation is the automotive and aerospace industry leader in the auto-dimming rear view mirror and electrochromic window shades in aircraft. The “Alteos”TM is the world’s first electrochromic window shades that are deployed in commercial aircraft Boeing 787 Dreamliner where passengers have the luxury to switch from a clear state to an extreme dark state with intermediate states by pressing a button [27]. Not surprisingly, the transportation and aerospace sector was projected to generate revenues of US\$1.9 billion in 2015 with 91.8% market share in the smart glass sector, according to BCC Research latest business report on smart glass [28].

16.1.1 Electrochromics for Green Buildings

Traditionally, mechanical blinds and shutters were used to reduce glare and incoming solar irradiation into buildings, which is not an efficient way of managing heat or temperature to maintain a comfortable temperature in the building. There is a need, therefore, for smart windows that are able to block incoming solar irradiation more efficiently than mechanical blinds and shutters [13, 29–31]. Smart windows are simply dynamic tintable glass that can change properties such as the solar heat gain coefficient (SHGC) and light transmittance in response to an electrical current/voltage. At present, various smart windows technologies are available in the market, namely, EC, liquid crystal (LC) and suspended-particle devices (SPD) or electrophoretic. Needless to say, one main

requirement of smart windows is that they must be able to reversibly change from the transparent state to the tinted state and vice versa.

In LC devices, the main mechanism of the optical states is the alteration in the orientation of the LC when an electric field is applied between two transparent electrodes, thereby changing the light transmittance through the device [32]. In this technology, the polymer-dispersed liquid crystals (PDLCs) and encapsulated liquid crystals (NCAP-nematic curvilinear aligned phase) are the most common [32–35]. Large-size PDLC windows are already available in the market in sizes of up to $1.0 \times 2.8 \text{ m}^2$ from Saint-Gobain glass [32]. As for the SPD devices, they are film based, consisting of 3–5 layers with an active layer containing adsorbing dipole-needle shaped polyhalides suspended in a gel/organic liquids in between two transparent conductors. Similar to LC devices, the dipole needles are randomly oriented in the off-state but will align and allow light to transmit through upon the application of an electric field. This technology has been patented by Research Frontiers Inc. and has recently been deployed in the Mercedes-Benz sunroofs called Magic Sky Control [36].

In Singapore, a nation that has tropical climate, the Singapore Green Building Council is focusing on technologies that can help to conserve energy consumption in buildings. According to the Building and Construction Authority (BCA) of Singapore, in 2014 over 38% of Singapore's electricity was consumed by Singapore's building sector [37]. Furthermore, the National Climate Change Secretariat (NCCS) of Singapore revealed that in 2014 on average, the air conditioning and mechanical ventilation (ACMV) could account for more than 50% of the total building energy consumption [38]. There is, therefore, a motivation to reduce the energy consumption of air conditioning in buildings. One of such a design consideration of a green building is to have an energy-efficient Building Envelope and Façade system (BEFS). The BEFS should be functional, rather than just a visual enclosure for buildings. Having a functional BEFS can potentially serve to redirect/filter solar irradiation into buildings, manage the heat transfer from outside environment into the building, create a natural ventilation, and improve the wellbeing of occupants through the visual and physical connection between the internal and external environments [38, 39].

According to a study conducted by Lawrence Berkeley National Laboratory, widespread use of EC windows in building fenestrations can reduce energy consumption of air conditioning in a building to as much as 26%, which makes it highly attractive for green building initiatives due to the low energy consumption and memory effect of such EC devices [40]. However, a report by National Renewable Energy Laboratory (NREL) revealed that the estimated cost of current EC windows available in the market is to be US\$50 to US\$100 per square foot (US\$538 to US\$1076 per square meter), which prevented its widespread adoption of the EC technology in the market. NREL also pointed out that the cost of smart windows has to go down to US\$20 per square foot (US\$215 per square meter) before it becomes attractive and cost-competitive enough for widespread adoption in residential market [41].

16.1.2 Electrochromics for Displays

The EC displays typically meet the key requirements of paper-based media such as readability, switching speed, power consumption, and stability to be considered as a replacement in the electronic display [42]. EC displays can operate either in reflectance or transmissive mode, or both, with the majority being the reflectance mode in display applications. EC is one of the most attractive candidates for paper-like displays, also known as electronic paper, which could be positioned as the next-generation display, owing to attributes, namely, low-power consumption, excellent ink-on-paper optical qualities, fast switching times, and thin and flexible materials [43–46]. EC displays are often termed “passive” as they do not emit light and require external illumination [47]. EC displays offer highly diffusive reflective property, high degree of independence viewing angle, high angle independent contrast, memory effect, readability under a wide range of illumination angles, and intensities of ambient light [42]. Such displays are expected to address diverse needs such as information signage, information tags, point-of-sale systems, advertising, switchable displays, e-readers, and mobile communications.

Display applications require different colors and/or at least three primary colors, which can result in other colors after mixing in order to obtain a wide range of colors. Two methods that are normally used to mix the colors are the additive RGB (red, green, and blue) and subtractive CMY (cyan, magenta, and yellow) [44, 48, 49]. A wide variety of colored pixels could be prepared by adding aqueous dye dispersions to the electrolyte to give vivid colors and can enhance the contrast ratios [50].

The impetus for the development of electrochromic paper is environmental cause. In principle, the electrochromes embedded within the sheet of paper can be reversibly switched between colored and bleached state, hence allowing the paper to be reused, rather than recycled [47]. In 1989, IBM introduced electrochromic paper that had the capability of producing multiple coloration, but the complexity of the system precluded economic commercialization of the product [47]. The earlier reflective display technologies required the use of color filters to provide a range of colors, which inherently reduced the amount of light reflected from the devices. Bach *et al.* noted the importance of chemically modified nanostructured electrode materials, which was the key to transforming electrochromics into a paper quality display technology, trademarking the technology under the name NanoChromics [43]. In their work, a white reflector (rutile titania or zinc oxide) was integrated into the device to provide a highly reflective background for the coloration. Corr *et al.* expanded the NanoChromics™ technology by using viologens that were modified with various alkyl substituents, giving rise to several materials in addition to the modified mesoporous titanium dioxide electrodes that acted as a mediator of the redox reaction [42]. This technology enabled device assembling in transparent mode, reflective mode, or a combination of both (transflective), which opened up the possibility of using backlighting and thus simplified the full color mixing. Monk *et al.* demonstrated a functional electrochromic paper by creating an image upon the touch of a stylus electrode in which the methyl viologens and

benzyl viologens electrochromes had been embedded in the paper [51, 52]. Yashiro *et al.* developed a full-color reflective electrochromic display based on the subtractive color mixing model featuring improved display brightness and color reproducibility [53]. The multilayered electrochromic display was designed to mimic the appearance of ordinary ink on paper by incorporating cyan, magenta, and yellow electrochromic inks, which could produce a wide range of colors through different combinations.

Another type of reflective EC devices can be fabricated via reversible electrodeposition, which does not require additional coating or layer and yet able to display electrochromic behavior. This can be achieved via reversible electrodeposition method, which involves the deposition and dissolution of a metal (Ag, Cu, Ni, Bi, Pb, and others) onto a transparent conducting substrate in order to modulate its optical properties [54–56]. These materials affect the color change via plating and dissolution of the thin films [57]. The electrochromic materials are dissolved in the electrolyte and form a thin film onto the substrate with the passage of electric current, and the film erasure takes place upon reverse bias, thereby affecting the optical modulation [58]. Potential applications include low information displays such as information signage and high information displays such as computer monitors, large-area tactile displays, and cockpit displays [50]. Reversible electrochemical mirrors (REMs) are designed to modulate their reflectance from a highly reflective state, enough to mirror a subject, to a highly transparent state in response to external stimuli such as electricity [54–56, 59]. Notable examples of these materials are silver [54–56] and viologens [60, 61]. Kobayashi group developed a novel, multifunctional ECD that incorporated both color changing and variable reflectance, which could be electrochemical optical-modulated between transparent, mirror, and black states via the electrodeposition of silver particles on flat ITO and ITO particle-modified electrode [54]. In the transparent state, the two-electrode EC device showed a reflectance of 20% and the reflectivity increased to almost 100% upon the bias voltage of -2.5 V beyond 500 nm. The EC device exhibited good optical modulation of 72% up to 2500 cycles, demonstrating high stability of the electrochemical deposition and dissolution. The multifunctional EC device together with its high switching stability offered wide potential applications in light-modulating devices such as smart windows and information displays.

Kim *et al.* also worked on silver-based EC and had addressed the issue of nonuniform deposition of Ag metal in the large-area displays by using cell partition method via the honeycomb structure [56]. The low open-circuit memory in switchable mirrors is inevitable as the electrodeposited metal particles are dissolved in the electrolytes that contained excess halide ions, which assist reversible switching. Thus, Park *et al.* provided a solution to an electrochemically stable and bistable switchable mirror by introducing a thiol-modified ITO electrode for the stabilization of the metallic Ag film and ionic liquids as an anion-blocking layer in order to obtain long memory effects of more than 2 h during the voltage-off state [55]. The long-term stability of the reflective state holds technological promise for applications such as optic devices, memory, displays, and energy-saving smart windows.

16.1.2.1 Solution Processing of Electrochromics

There are intense efforts in fabricating electrochromic devices using cost-effective solution-processable coating techniques spanning from spray-coating [44–46], electrochemical polymerization [48], electrochemical deposition [49, 62, 63], spin-coat [64–66], slot-die coating [67], roll coating [68–70], screen printing [71], layer-by-layer self-assembly [72], hydrothermal [73, 74], solvothermal [75], solution-casting polymerization [76], to REMs [54–56]. These solution methods are versatile compared to vacuum deposition and could provide the key ingredient for printing technologies. In this section, we review the progresses in electrochromics fabrication using solution-processable techniques.

Polymeric electrochromes are attractive for transmissive/reflective ECs and displays as they offer fast response time, high contrast ratio, high coloration efficiency, mechanical flexibility, long-term redox stability, solution processability, and a range of colors spanning the full visible spectrum, along with color tunability through structural control [44, 45]. Reynolds' group has discussed on the main classes of electrochromic organic and polymeric materials for display applications, namely, the transition metal coordination complexes, viologen systems, and conducting polymers [44–46, 77]. One of the highlight of their works is the low-voltage switching of π -conjugated polymer electrochromes, 3,4-propylenedioxythiophene (ProDOT). This spray-processable ProDOT can be cathodically colored to reach the saturated-blue state and oxidize to the highly transmissive state via the donor–acceptor approach [46]. Another interesting work that is based on the donor–acceptor approach delivers the promising black-to-transmissive electrochromic polymers (ECPs) for both transmissive and reflective EC devices. This allows lower processing costs through printing, spraying, and coating methods, along with good scalability [44]. The polymer P9 was synthesized from 3,3-bis(2-ethylhexyloxy)methyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepine-6-yl)trimethyl-stannane, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole, bis(triphenylphosphine)palladium(II) dichloride in toluene, followed by mixing the product with 3,3-bis-(2-ethylhexyloxy)methyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepine in chloroform. The spray-casted P9 film exhibited deep black color in its neutral state, attained transmittance change of 51.5% on electro-oxidation, and demonstrated outstanding stability by achieving long-term switching of 10 000 cycles. Meanwhile, a side-chain defunctionalization approach yielded a polymer electrochrome spray-processable from water in which simple homopolymer of 3,4-propylenedioxythiophene (ProDOT) was used as a platform test, and π -conjugated polymer electrochromes bearing alkyl ester side chains were chemically synthesized and subsequently defunctionalized to yield low aliphatic content of polycarboxylate salts that were readily soluble in water [45]. The spray-casted PProDOT-acid exhibited optical transmittance contrast of about 60% at switching rates ranging from 10 to 0.5 s and at the same time demonstrated excellent redox stability over 16 000 cycles with less than 5% contrast variation. These nonemissive organic electrochromes offered cost-effective solution processing over large-area and mechanically deformable surfaces, ambient condition processing, and nontoxic and high-throughput manufacturing conditions, which could rapidly take ECPs to the forefront of organic electronics with commercial applicability [44–46].

Toppare group developed donor–acceptor-type ECPs with the objective of completing the RGB color space by synthesizing the neutral green materials, poly[2,3-bis(4-*tert*-butylphenyl)-5,8-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7yl)quinoxaline (PTBPEQ) and poly[2,3-diphenyl-5,8-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-7-yl)quinoxaline (PDPEQ) that exhibit exceptional transmissive oxidized states [48]. Both electropolymerized polymers revealed excellent optical contrast of 95% in the visible region, especially PTBPEQ, which was highly transmissive in the oxidized state, and showed optical contrast of 77% in the NIR region and long-term stability up to 5000 cycles, along with fast switching times of less than 1 s, making these polymers the paramount choices for the green component of polymer electrochromic display applications. Assis *et al.* reported on all solid-state green-yellow reflective EC device built with electrodeposited Prussian blue (PB) as the electrochromic layer [49]. Based on the subtractive two colors mixing method, the EC device changed its reflectance from 46% (at -2 V) to 23% ($+2$ V) at the wavelength of 550 nm. Kim's group prepared solution-casting polymerization and photopatterning of poly(3,4-alkylenedioxythiophene) (PXPOT) derivatives, which were useful for flexible large-sized electrochromic displays [76]. The electrochromic display was electroswitchable from a colored state to the bleached state with the highest attainable contrast of 45.7%.

Our group reported spin coating of an anodically coloring electrochromic conducting polymer, polyaniline with dodecylbenzene sulfonic acid (PANI–DBSA). The flexible, reflective EC device had the device configuration of PANI–DBSA/gold-coated membrane/electrolyte/poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate)(PEDOT:PSS)/aluminum foil. With the solid poly(vinylidene fluoride-trifluoroethylene)/polyethylene oxide (P(VDF-TrFE)/PEO)-based polymer electrolyte, the device achieved a dynamic reflectance modulation of about 50% when the device was cycled between -1.5 and $+0.5$ V [66]. With the successful incorporation of solid polymer electrolyte in the reflective device, this would expedite the development of flexibility display applications.

Inorganic electrochromic materials are rich in their structure–property diversification and have recently made significant progress in being tailored into nanostructures such as nanoparticles [78–80], nanorods [74, 81, 82], nanowires [17, 83–85], and core–shell structure with a conductive material as the core and a thin layer of electrochromic material as the shell [86, 87]. The large surface-to-volume ratio enhanced EC properties of the resultant EC devices, such as bleaching time, coloring time, and coloration efficiency, compared to the electrochromic performances of thin films [87, 88]. This has driven much efforts in the preparation of EC nanomaterials especially the transition metal oxide (TMO) nanostructures due to their multiple oxidation states and the possibilities of assembly of nanostructures to form high-quality thin films. One of the examples is our pioneering work in synthesizing scalable WO_3 nanorods and its assembly into electrochromic electrodes [73]. The nanostructured oxide layer formed is typically porous, and this allows facile electrolyte penetration. A reduced ionic diffusion length can be achieved for effective ion transport, and a larger amount of electrochemical reaction sites are available due to the higher surface area. These factors have direct impact on the faster switching

kinetics of the inorganic ECs. The outstanding electrochromic performances can be realized with porous WO_3 films formed using pulsed electrochemical depositions testifying the importance of complete infiltration of electrolyte into the porous structure with enhanced electrochemical activity, as we validate recently with the ultra-high transmittance modulation at near ideal 97.7% at 633 nm [19].

In addition, the modulation of the optical absorption bands can be achieved by doped TMOs by varying the ratio of the constituent oxides and consequently modifying the electronic structure. For example, molybdenum-doped WO_3 was found to have improved ion diffusion coefficient in thin films due to increased crystalline disorder [89]. Recently, we have shown that an *in situ* oxidation spray coating of preformed tungsten molybdenum oxide nanoparticle ink is effective to promote intimate contacts between EC material and electrolyte/current collector, improving the EC performance [90]. The progress on the solution processing of electrochromics has exerted some influence and led to the further development of printable electrochromics.

16.1.2.2 Printing Techniques in Electrochromics

There are at present many printing techniques that can be used in manufacturing due to their simple process, low cost, and easy industrialization. One embodiment of particular interest is the various printing techniques available for electrochromics, such as screen printing, inkjet printing, flexographic printing, roll-to-roll printing press, slot die, rotogravure, and doctor blade printing. Ink preparation and formulation is one of the key components that will affect the printing process. In this section, we review the recent progresses in printing techniques for preparing electrochromics.

16.2 Screen Printing

Screen printing is an additive patterning method in which a mesh is used to transfer desired material onto a substrate. It is often used as a flat printing technique in batch process. A blade is moved across the screen to fill the open mesh apertures with ink, except for areas impermeable to the ink by a blocking stencil. It is a very versatile printing technique that has advantages of high reproducibility, design flexibility, wide choice of materials, and the potential for mass production [91]. It includes a series of basic procedures, such as screen selection, inks preparation, substrate selection, drying, and curing. The inks applied in the screen-printing technology are required to have a relatively high viscosity (10^3 to 10^4 cP) and a low volatility of the coating solution, and need to be solidified and dried through a thermal treatment. To date, numbers of inorganic and organic electrochromic films were fabricated by screen printing technique. Most of the devices prepared by screen printing technique contain white pigment particles, which provide a highly reflective background; hence, they are mainly used for reflective displays and electronic paper. Coleman *et al.* used screen printing technique to develop some displays such as bismuth-based display,



Figure 16.2 Antimony-doped tin oxide-based display by applying a voltage window of ± 1.5 V. (Liu and Coleman (2000) [92]. Reproduced with permission of Elsevier.)

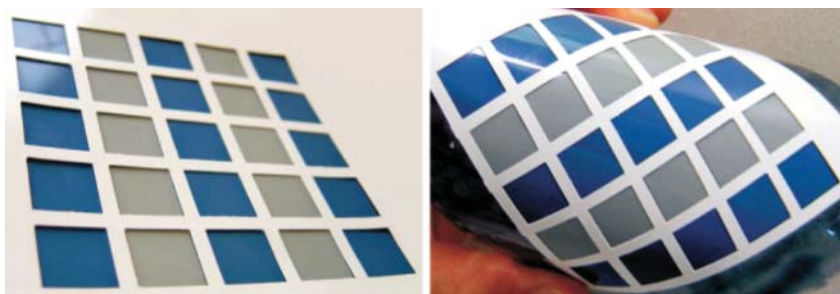


Figure 16.3 PEDOT:PSS-based active-matrix display prepared by screen printing methods. (Andersson *et al.* (2007) [95]. Reproduced with permission of Wiley.)

Prussian blue-based display, and antimony-doped tin oxide-based display as shown in Figure 16.2 [92–94]. These displays exhibit fast switching speed (within 10 s) and more than 20% reflectance modulation under a voltage window of ± 1.5 V. Berggren *et al.* developed the organic matrix displays using screen printing method based on poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) as shown in Figure 16.3 [71, 95–97]. These organic matrix displays present large color contrast and relatively short switching time (less than 1 s) at an operational voltage less than 2 V. In order to improve the electrochromic performances, the displays based on inorganic–organic composites were fabricated by screen printing techniques [98, 99]. The electrochromic layer in both works was prepared via adsorbed viologen molecules on the surface of the nanocrystalline TiO_2 . The displays based on TiO_2 /viologen composites prepared by screen printing present fast response times (within 0.5 s) under low driving voltage (-1.2 V) and long-term stability (35 000 cycles).

16.3 Inkjet Printing

Inkjet printing is one common digital printing method for printing computer text and images onto paper. In the past decades, inkjet printing has progressed from printing text and images to a well-established technique to print functional materials. Inkjet printing is a precise and noncontact direct write technology with the obvious advantages of low-cost, high-resolution patterns, efficient use of materials, and being applicable to a variety of substrates. However, the inkjet printing has strict physicochemical property requirements for inks [100, 101]. Apart from the basic requirements such as long-term stability, friendly to human health and environment, the inks used for inkjet printing should also have appropriate viscosity, surface tension, and maximum particle size. Usually, the viscosity of the inks used for inkjet printing is in the range of 1–50 cP, lower than that of the screen printing ink, allowing smooth delivery of the ink between the cartridge and the printer head. The surface tension should be higher than 20 mN m^{-1} , which can make the ink wetting well the faceplate around the nozzles and the ink drops spread well over the substrates. The maximum nanoparticle size should be at least several decade times smaller than the nozzle diameter to avoid blocking the nozzles. Therefore, maximum particle size should be ideally less than 500 nm due to the typical nozzle diameter is in the range of tens of micrometers.

As an emerging films preparation technology, inkjet printing of electrochromic films has gained more and more attention during the past 10 years. It allows deposition of electrochromic materials on a specific location in addition to thickness control by the number of printed layers. Until now, many organic and inorganic electrochromic devices were fabricated by inkjet printing technique with potential applications such as displays and smart windows. Möller *et al.* [102] have first reported on organic electrochromic displays with a high resolution of 360 dpi prepared by inkjet printing. The displays based on viologen show switching time in the range of 2 s and good long-term stability. Shim *et al.* [103] have synthesized polyaniline (PANI)–silica and PEDOT–silica colloidal composite particles with a diameter of 200–300 nm, which were then converted into intrinsically conducting polymer inks via solvent exchange with viscosity of 12 cP and surface tension of 23 mN m^{-1} . The electrochromic devices were fabricated using inkjet-printed conducting polymer electrochromic layer, which exhibited varied colored changes corresponding to the potentials applied. Recently, inkjet-printed multicolored electrochromic devices based on metallo-supramolecular polymers were studied by Chen *et al.* [104]. The printed electrochromic devices exhibited great contrast with a transmittance change (ΔT) of 40.1% and a high coloration efficiency of $445 \text{ cm}^2 \text{ C}^{-1}$ within a short switching time of 2 s between a voltage range of $\pm 3 \text{ V}$.

Besides the inkjet-printed organic electrochromic devices, inkjet-printed inorganic electrochromic devices are attracting more and more attention in the past 5 years. Application of inorganic metal oxide nanoparticles synthesized and formulated with the technical specifications for inkjet printing is more difficult

than that of the organic semiconductor polymers because inkjet printing inks should be made of particles with sizes small enough so that they do not damage the printer nozzles. Therefore, the metal oxide nanoparticles with small sizes are prepared usually by sol–gel, hydrothermal, and solvothermal methods. Costa *et al.* [25, 105] have assembled solid-state symmetric electrochromic devices using the inkjet-printed WO_3 and V_2O_5 films, respectively. In their work, both WO_3 nanoparticles and V_2O_5 ribbons with a size of about 200 nm were prepared by sol–gel methods, and the viscosity and surface tension of both inks are almost the same, which are 2 cP and 60 mN m^{-1} . Both electrochromic cells show excellent contrast between the redox states and good cycling stability up to more than 10^4 cycles. Vidmar *et al.* [24] have reported on inkjet-printed electrochromic WO_3 layers using a sol–gel-derived tungsten inks with viscosity less than 11.1 cP and surface tension about 25 mN m^{-1} . The electrochromic device exhibits an optical contrast of 53% between potential ranges of -1.5 to 1.0 V and switching characteristic within a few seconds (3–7 s). Meanwhile, Fortunato's group has provided an effective means to explore and predict the behavior of high-performance EC devices by a combination of inkjet printing method and the design of experiment methodology [106–109]. Their results revealed dual-phase films deposited by inkjet printing method have higher values of transmission modulation over the visible and near-infrared regions compared to the poor EC performance of single-phase amorphous films. Although the printed electrochromic layers were successfully fabricated by inkjet printing technique in the aforementioned publications, the cracks and discontinuous film often appeared in the electrochromic layers. Recently, we have fabricated an all solid-state electrochromic device based on inkjet-printed NiO and WO_3 complementary electrodes [26]. The NiO and WO_3 nanoparticles with small size were prepared by solvothermal and sol–gel methods, respectively. A versatile ink formulation was successfully developed for NiO and WO_3 nanoparticles with surface tension and viscosity of 23 mN m^{-1} and 7 cP, respectively, and the continuous electrochromic films without aggregation were successfully prepared using inkjet printing method. After annealing at 200°C for 2 h to evaporate the organic solvent, the porous NiO film with nine printed layers exhibits an optical modulation of 64.2% at 550 nm and a coloration efficiency of $136.7 \text{ cm}^2 \text{ C}^{-1}$. In addition, the inkjet-printed complementary all solid-state device exhibits a large optical modulation of 75.4% at 633 nm and a high coloration efficiency of $131.9 \text{ cm}^2 \text{ C}^{-1}$ because the printed NiO film performs not only as an ion storage layer but also as a complementary electrochromic layer (Figure 16.4). Besides ITO/FTO-based electrochromic devices, the electrochromic devices with ITO/FTO free were fabricated by inkjet printing technique. For example, we have fabricated WO_3 electrochromic films onto a transparent and flexible silver grid/PET substrate via inkjet printing [23]. The contrast of the electrochromic device can be tailored by controlling the number of printed layers and the concentration of WO_3 nanoparticles in the ink. The highest contrast achieved under optimal conditions was found to be as high as 72% (Figure 16.4) [26]. Patterning using inkjet printing can be achieved as shown in Figure 16.5.

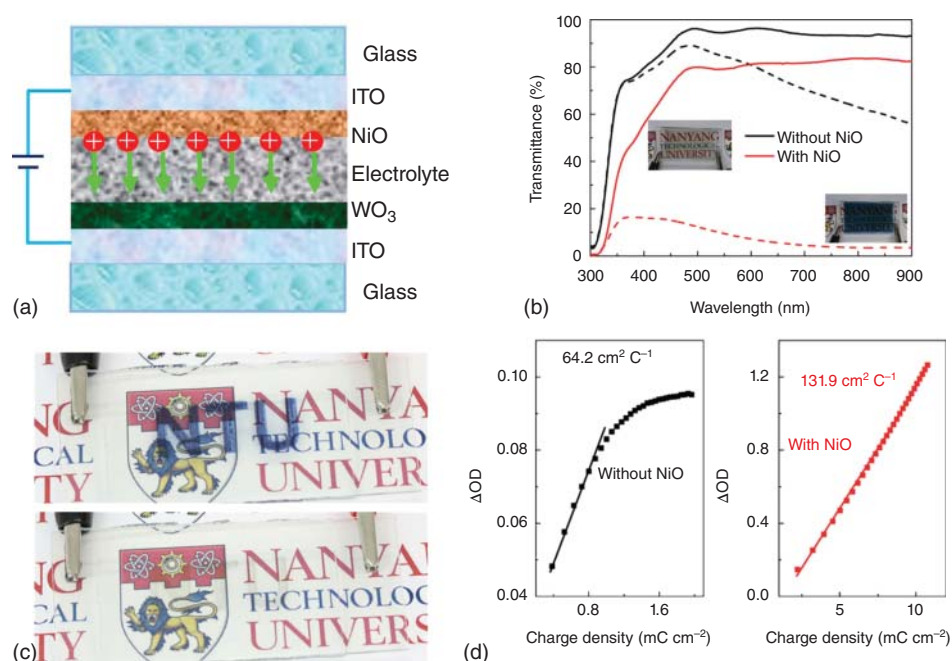


Figure 16.4 (a) Setup of inkjet-printed solid electrochromic device; (b) transmittance spectra of the solid electrochromic device with and without NiO as ion storage layer in the bleached and colored states; (c) a photograph of the pattern solid device with NiO as ion storage layer; (d) the variation of the *in situ* optical density (ΔOD) versus the charge density for the solid electrochromic device with and without NiO as ion storage layer. (Cai *et al.* (2016) [26]. Reproduced with permission of Royal Society of Chemistry.)

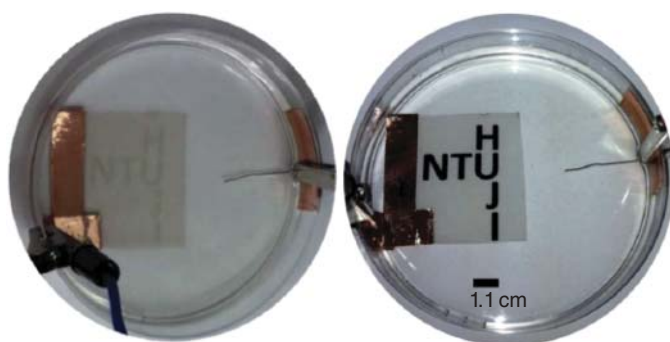


Figure 16.5 Electrochromic cell with a transparent silver grid electrode and a Pt counter electrode dipped into the LiClO_4/PC electrolyte. (Layani *et al.* (2014) [23]. Reproduced with permission of Royal Society of Chemistry.)

16.4 Flexographic Printing

Flexographic printing is a high-throughput technique with excellent reproducibility, which involves a flexible rubber or polymer printing plate. Ink applied to the plate cylinder may be water or solvent based with low to medium viscosity. Until now, there was no published work on electrochromic layer made by flexographic printing methods, but some flexible transparent electrodes were fabricated by flexographic printing technique [110–112]. Krebs's group has assembled flexible electrochromic devices based on the flexoprinted silver grid as transparent conductive substrates [64, 67, 113]. The flexible electrochromic devices exhibit an optical modulation of about 30% and a switching speed of about tens of seconds.

16.5 Roll-to-Roll Printing

Roll-to-roll printing is one of the industrialized coating methods to obtain rapidly produced large-area films with low costs and excellent durability. It is expected that roll-to-roll processing will greatly reduce the cost of electrochromic devices and allow significant market penetration for electrochromism. Usually, the roll-to-roll technique includes coating electrochromic materials on flexible substrates and then followed by continuous lamination. Widjaja *et al.* have fabricated a good performing electrochromic device by depositing WO_3 on ITO/PET substrate by a continuous mode in the roll coater [114]. The flexible device shows an optical modulation over 45% and a switching time of about 20 s. Moreover, some organic displays were also prepared by roll-to-roll technique and exhibited good electrochromic performance, such as dihexyl-substituted poly(3,4-propylenedioxythiophene) (PProDOT-Hx₂) [115] and PEDOT:PSS [95]-based displays. The complicated pattern can be achieved by the combination of roll-to-roll, screen printing, and other methods. As previously mentioned, Krebs's group has assembled the flexible electrochromic devices by the combination of many coating methods such as roll-to-roll, flexographic printing, slot-die, and spin coating [64, 67, 113]. Besides the traditional electrochromic materials, Polat *et al.* [70] have prepared graphene-based electrochromic devices by roll-to-roll fabrication. Large-area multilayer graphene on metal foils was synthesized by chemical vapor deposition, and then laminated by polyvinyl chloride (PVC) films on the graphene-coated side of the foils; finally, etching the foils can yield large-area graphene films on the transparent and flexible substrate. The graphene-based electrochromic devices can be used for reflective transmissive multipixel displays and have high optical contrast (55%) and fast switching speed (within 3.5 s).

16.6 Other Printing Methods

Of course, there are many other printing and coating techniques that can be potentially used to fabricate electrochromic devices, such as spray layer-by-layer,

slot die, rotogravure, and doctor blade printing. However, they are not the main methods used at present for the fabrication of electrochromic devices. The process of these methods is not discussed in detail here.

16.7 Conclusions and Perspectives

To achieve versatile emerging applications, there are ongoing efforts on imparting attractive features such as mechanical flexibility, stretchability, and foldability properties in electrochromic devices. This can be accomplished by replacing the rigid indium tin oxide (ITO) glass or fluorine-doped tin oxide (FTO) glass with flexible electrodes such as ITO on poly(ethylene terephthalate) (PET) and silver (Ag) grids/rings on PET substrates. The brittleness of the ITO makes it unsuitable for flexible device applications, and its high cost is a pitfall in the economic commercialization of the electrochromics. With the flexible or stretchable features, diverse wearable EC applications such as biomimicry, adaptive camouflage, wearable displays, and fashion can be imagined. For instance, the electrochromic fabric devices with fully integrated fabrics could revolutionize fashion, and the designs could be infinite and could set a new trend toward human advertising [116]. For example, an all-printed passive matrix addressed electrochromic displays (PMAD) using PEDOT:PSS held promises for high-volume and low-cost production of flexible displays using reel-to-reel printing tools on paper or plastic foils [23]. It can be adoptable in wide applications such as distributed diagnosis, home healthcare, or sensor platforms, which could be used to monitor the status of perishable goods in logistic chains. Our group has used silver grid/PEDOT:PSS to replace ITO as flexible transparent conductors. This hybrid substrate delivers large optical modulation in the electrodeposited WO_3 nanoparticles, excellent cycling stability (sustaining 79.1% of their initial transmittance modulation after 1000 cycles), and remarkable mechanical flexibility (optical modulation decay only 7.5% after 1200 compression bending cycles). Remarkably, it is bifunctional with its simultaneous charge/discharge energy storage during reversible color variation as an electrochromic-supercapacitor [20].

Notably, our group has demonstrated stretchable and wearable electrochromics by electrochemically deposited WO_3 onto the silver nanowire/polydimethylsiloxane (AgNW/PDMS) elastic conductor [63]. The stretchable ECDs were mechanically robust and could be stretched, twisted, folded, and crumpled. The device exhibited a reflectance contrast of 56% at 633 nm at the relaxed state, 50% reflectance contrast at the stretched state (50% strain applied), fast coloration time of 1 s, and bleaching time of 4 s besides good cycling stability. As a proof of concept, the wearable ECDs were implanted onto a cotton textile substrate to demonstrate the feasibility of addressing the individual pixels separately or in any combinations as shown in Figure 16.6. In addition, we extended our efforts on realizing foldable electrochromics can be achieved using nanocellulose paper incorporated with metallic Ag nanowires as the transparent conductors

Figure 16.6 (a) Schematic of the electrochromic electrode implanted onto wearable textiles; (b) example images showing the capability to control the coloration/bleaching of individual display pixels and their mechanical stabilities against deformations such as crumpling. Scale bar for display pixels: 2 mm. (Yan *et al.* (2014) [63]. Reproduced with permission of American Chemical Society.)

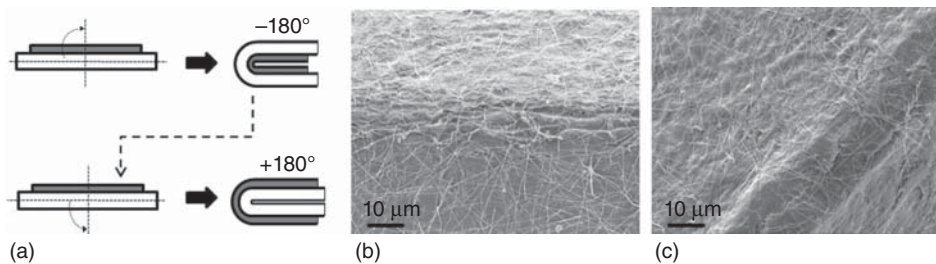
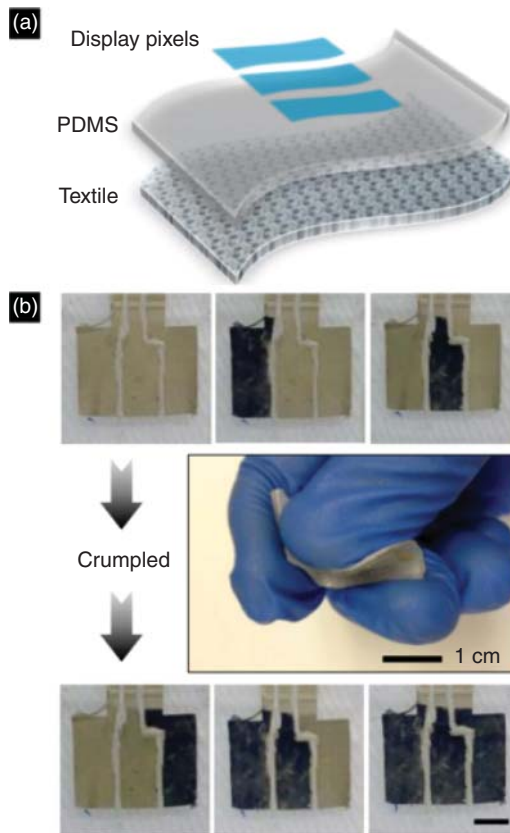


Figure 16.7 Foldability test of nanopaper. (a) Schematics for the folding procedure; FESEM images of the nanopaper electrode folded to (b) 180° and (c) +180°. (Kang *et al.* (2015) [117]. Reproduced with permission of Wiley.)

(Figure 16.7), the foldable EC device is operational even after 50 cycles of folding [117]. These innovative EC devices in their soft form hold the promise for the next-generation electronics especially for the stretchable, wearable, and implantable or foldable display applications or wearable display panels implanted on clothes and skin.

References

- 1 Davenport, C., *Nations Approve Landmark Climate Accord in Paris*. Available: http://www.nytimes.com/2015/12/13/world/europe/climate-change-accord-paris.html?_r=0 (accessed 18 August 2016).
- 2 <http://www.cop21paris.org> (accessed 18 August 2016).
- 3 AFP. *The Guardian, World's richest 10% produce half of global carbon emissions, says Oxfam*. Available: <http://www.theguardian.com/environment/2015/dec/02/worlds-richest-10-produce-half-of-global-carbon-emissions-says-oxfam> (accessed 18 August 2016)
- 4 Thakur, V.K., Ding, G., Ma, J., Lee, P.S., and Lu, X. (2012) Hybrid materials and polymer electrolytes for electrochromic device applications. *Adv. Mater.*, **24**, 4071–4096.
- 5 Higuchi, M. (2009) Electrochromic organic-metallic hybrid polymers: Fundamentals and device applications. *Polym. J.*, **41**, 511–520.
- 6 Beaujuge, P.M., Amb, C.M., and Reynolds, J.R. (2010) Spectral engineering in π -conjugated polymers with intramolecular donor–acceptor interactions. *Acc. Chem. Res.*, **43**, 1396–1407.
- 7 Deb, S.K. (1969) A novel electrophotographic system. *Appl. Opt. Suppl.*, **3**, 192–195.
- 8 Granqvist, C.G. (1995) *Handbook of Inorganic Electrochromic Materials*, Elsevier.
- 9 Platt, J.R. (1961) Electrochromism, a possible change of color producible in dyes by an electric field. *J. Chem. Phys.*, **34**, 862–863.
- 10 Niklasson, G.A. and Granqvist, C.G. (2007) Electrochromics for smart windows: Thin films of tungsten oxide and nickel oxide, and devices based on these. *J. Mater. Chem.*, **17**, 127–156.
- 11 Baloukas, B., Lamarre, J.M., and Martinu, L. (2011) Electrochromic interference filters fabricated from dense and porous tungsten oxide films. *Sol. Energy Mater. Sol. Cells*, **95**, 807–815.
- 12 Wang, C.-K., Lin, C.-K., Wu, C.-L., Brahma, S., Wang, S.-C., and Huang, J.-L. (2013) Characterization of electrochromic tungsten oxide film from electrochemical anodized RF-sputtered tungsten films. *Ceram. Int.*, **39**, 4293–4298.
- 13 Granqvist, C.G. (2014) Electrochromics for smart windows: Oxide-based thin films and devices. *Thin Solid Films*, **564**, 1–38.
- 14 Bertus, L.M., Faure, C., Danine, A., Labrugere, C., Campet, G., Rougier, A. *et al.* (2013) Synthesis and characterization of WO₃ thin films by surfactant assisted spray pyrolysis for electrochromic applications. *Mater. Chem. Phys.*, **140**, 49–59.
- 15 Li, C.-P., Wolden, C.A., Dillon, A.C., and Tenent, R.C. (2012) Electrochromic films produced by ultrasonic spray deposition of tungsten oxide nanoparticles. *Sol. Energy Mater. Sol. Cells*, **99**, 50–55.
- 16 Tung, T.-S., Chen, L.-C., and Ho, K.-C. (2003) An indium hexacyanoferrate–tungsten oxide electrochromic battery with a hybrid K⁺/H⁺-conducting polymer electrolyte. *Solid State Ionics*, **165**, 257–267.

- 17 Gubbala, S., Thangala, J., and Sunkara, M.K. (2007) Nanowire-based electrochromic devices. *Sol. Energy Mater. Sol. Cells*, **91**, 813–820.
- 18 White, C.M., Gillaspie, D.T., Whitney, E., Lee, S.-H., and Dillon, A.C. (2009) Flexible electrochromic devices based on crystalline WO_3 nanostructures produced with hot-wire chemical vapor deposition. *Thin Solid Films*, **517**, 3596–3599.
- 19 Cai, G., Cui, M., Kumar, V., Darmawan, P., Wang, J., Wang, X. *et al.* (2016) Ultra-large optical modulation of electrochromic porous WO_3 film and the local monitoring of redox activity. *Chem. Sci.*, **7**, 1373–1382.
- 20 Cai, G., Darmawan, P., Cui, M., Wang, J., Chen, J., Magdassi, S. *et al.* (2015) Highly stable transparent conductive silver grid/PEDOT:PSS electrodes for integrated bifunctional flexible electrochromic supercapacitors. *Adv. Energy Mater.*, **6**, 1501882.
- 21 Chen, X. and Mao, S.S. (2007) Titanium Dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chem. Rev.*, **107**, 2891–2959.
- 22 Leftheriotis, G., Koubli, E., and Yianoulis, P. (2013) Combined electrochromic-transparent conducting coatings consisting of noble metal, dielectric and WO_3 multilayers. *Sol. Energy Mater. Sol. Cells*, **116**, 110–119.
- 23 Layani, M., Darmawan, P., Foo, W.L., Liu, L., Kamyshny, A., Mandler, D. *et al.* (2014) Nanostructured electrochromic films by inkjet printing on large area and flexible transparent silver electrodes. *Nanoscale*, **6**, 4572–4576.
- 24 Vidmar, T., Topič, M., Dzik, P., and Opara Krašovec, U. (2014) Inkjet printing of sol–gel derived tungsten oxide inks. *Sol. Energy Mater. Sol. Cells*, **125**, 87–95.
- 25 Costa, C., Pinheiro, C., Henriques, I., and Laia, C.A.T. (2012) Inkjet printing of sol–gel synthesized hydrated tungsten oxide nanoparticles for flexible electrochromic devices. *ACS Appl. Mater. Interfaces*, **4**, 1330–1340.
- 26 Cai, G., Darmawan, P., Cui, M., Chen, J., Wang, X., Eh, A.L.-S. *et al.* (2016) Inkjet-printed all solid-state electrochromic devices based on NiO/WO_3 nanoparticle complementary electrodes. *Nanoscale*, **8**, 348–357.
- 27 G. Corporation. Available: <http://www.gentex.com>
- 28 BCC Research, Global Markets and Technologies for Smart Glass, *AVM065C*, 2015.
- 29 Smith, G.B. and Granqvist, C.G.S. (2010) *Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment*, CRC Press, Boca Raton, FL, USA.
- 30 García-Martínez, J. (2013) *Nanotechnology for Energy Challenge*, 2nd edn, Wiley-VCH, Weinheim, Germany.
- 31 Pacheco-Torgal, M.V.D.F., Nazari, A., and Granqvist, C.G. (2013) *Nanotechnology in Eco-efficient Construction*, Woodhead, Cambridge, UK.
- 32 Baetens, R., Jelle, B.P., and Gustavsen, A. (2010) Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review. *Sol. Energy Mater. Sol. Cells*, **94**, 87–105.
- 33 Lampert, C.M. (1998) Smart switchable glazing for solar energy and daylight control. *Sol. Energy Mater. Sol. Cells*, **52**, 207–221.

- 34 Lampert, C.M. (2003) Large-area smart glass and integrated photovoltaics. *Sol. Energy Mater. Sol. Cells*, **76**, 489–499.
- 35 Lampert, C.M. (2004) Chromogenic smart materials. *Mater. Today*, **7**, 28–35.
- 36 R. *Frontiers*. Available: <http://www.smartglass.com> (accessed 18 August 2016)
- 37 BCA. (2015). *BCA Building Energy Benchmarking Report 2014*. Available: http://www.bca.gov.sg/GreenMark/others/BCA_BEER_Abridged_FA.pdf (accessed 18 August 2016)
- 38 NCCS. (2014). *Building Energy Efficiency R&D Roadmap*. Available: https://www.nccs.gov.sg/sites/nccs/files/Roadmap_BEE_20140729.pdf (accessed 18 August 2016)
- 39 Hegger, M.F.M., Stark, T., and Seumer, M. (2007) *Energie Atlas - Nachhaltige Architektur*, Birkhäuser, Berlin, Germany.
- 40 Bhuvana, T., Kim, B., Yang, X., Shin, H., and Kim, E. (2013) Reversible full-color generation with patterned yellow electrochromic polymers. *Angew. Chem. Int. Ed.*, **52**, 1180–1184.
- 41 Roberts, D. R., Preliminary Assessment of the Energy Saving Potential of Electrochromic Windows in Residential Buildings, *Technical Report NREL*, TP-550-469162009.
- 42 Corr, D., Bach, U., Fay, D., Kinsella, M., McAtamney, C., O'Reilly, F. *et al.* (2003) Coloured electrochromic “paper-quality” displays based on modified mesoporous electrodes. *Solid State Ionics*, **165**, 315–321.
- 43 Bach, U., Corr, D., Lupo, D., Pichot, F., and Ryan, M. (2002) Nanomaterials-based electrochromics for paper-quality displays. *Adv. Mater.*, **14**, 845–848.
- 44 Beaujuge, P.M., Ellinger, S., and Reynolds, J.R. (2008) The donor–acceptor approach allows a black-to-transmissive switching polymeric electrochrome. *Nat. Mater.*, **7**, 795–799.
- 45 Beaujuge, P.M., Amb, C.M., and Reynolds, J.R. (2010) A side-chain defunctionalization approach yields a polymer electrochrome spray-processable from water. *Adv. Mater.*, **22**, 5383–5387.
- 46 Amb, C.M., Beaujuge, P.M., and Reynolds, J.R. (2010) Spray-processable blue-to-highly transmissive switching polymer electrochromes via the donor–acceptor approach. *Adv. Mater.*, **22**, 724–728.
- 47 Monk, P., Mortimer, R., and Rosseinsky, D. (2007) *Electrochromism and Electrochromic Devices*, Cambridge University Press.
- 48 Gunbas, G.E., Durmus, A., and Toppare, L. (2008) Could green be greener? novel donor–acceptor-type electrochromic polymers: Towards excellent neutral green materials with exceptional transmissive oxidized states for completion of RGB color space. *Adv. Mater.*, **20**, 691–695.
- 49 Assis, L.M.N., Ponez, L., Januszko, A., Grudzinski, K., and Pawlicka, A. (2013) A green-yellow reflective electrochromic device. *Electrochim. Acta*, **111**, 299–304.
- 50 Howard, B.M. and Ziegler, J.P. (1995) Optical properties of reversible electrodeposition electrochromic materials. *Sol. Energy Mater. Sol. Cells*, **39**, 309–316.

- 51 Monk, P.M.S., Turner, C., and Akhtar, S.P. (1999) Electrochemical behaviour of methyl viologen in a matrix of paper. *Electrochim. Acta*, **44**, 4817–4826.
- 52 Monk, P.M.S., Delage, F., and Costa Vieira, S.M. (2001) Electrochromic paper: Utility of electrochromes incorporated in paper. *Electrochim. Acta*, **46**, 2195–2202.
- 53 Yashiro, T., Hirano, S., Najjoh, Y., Okada, Y., Tsuji, K., Abe, M. *et al.* (2011) 5.3: Novel design for color electrochromic display. *SID Int. Symp. Dig. Tech. Pap.*, **42**, 42–45.
- 54 Araki, S., Nakamura, K., Kobayashi, K., Tsuboi, A., and Kobayashi, N. (2012) Electrochemical optical-modulation device with reversible transformation between transparent, mirror, and black. *Adv. Mater.*, **24**, OP122-6, OP121.
- 55 Park, C., Seo, S., Shin, H., Sarwade, B.D., Na, J., and Kim, E. (2015) Switchable silver mirrors with long memory effects. *Chem. Sci.*, **6**, 596–602.
- 56 Kim, T.-Y., Cho, S.M., Ah, C.S., Suh, K.-S., Ryu, H., and Chu, H.Y. (2014) Electrochromic device for the reversible electrodeposition system. *J. Inf. Disp.*, **15**, 13–17.
- 57 Ziegler, J.P. and Howard, B.M. (1995) Applications of reversible electrodeposition electrochromic devices. *Sol. Energy Mater. Sol. Cells*, **39**, 317–331.
- 58 deTorres, S.I.C. and Carlos, I.A. (1996) Optical characterization of bismuth reversible electrodeposition. *J. Electroanal. Chem.*, **414**, 11–16.
- 59 Hikmet, R.A.M. and Kemperman, H. (1998) Electrically switchable mirrors and optical components made from liquid-crystal gels. *Nature*, **392**, 476–479.
- 60 Edsberg, R.M.E.a.R.L. (1957) Polarographic behavior of the viologen indicators. *Can. J. Chem.*, **35**, 646–650.
- 61 Fish, G.G.B.a.J.G. (1981) An improved electrochromic display using an assymmetrical viologen. *J. Electrochem. Soc.*, **128**, 1290–1292.
- 62 Liu, L., Layani, M., Yellinek, S., Kamyshny, A., Ling, H., Lee, P.S. *et al.* (2014) “Nano to nano” electrodeposition of WO₃ crystalline nanoparticles for electrochromic coatings. *J. Mater. Chem. A*, **2**, 16224–16229.
- 63 Yan, C., Kang, W., Wang, J., Cui, M., Wang, X., Foo, C.Y. *et al.* (2014) Stretchable and wearable electrochromic devices. *ACS Nano*, **8**, 316–322.
- 64 Jensen, J., Hösel, M., Kim, I., Yu, J.-S., Jo, J., and Krebs, F.C. (2014) Fast switching ITO free electrochromic devices. *Adv. Funct. Mater.*, **24**, 1228–1233.
- 65 Heuer, H.W., Wehrmann, R., and Kirchmeyer, S. (2002) Electrochromic window based on conducting poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate). *Adv. Funct. Mater.*, **12**, 89–94.
- 66 Nguyen, C.A., Xiong, S., Ma, J., Lu, X., and Lee, P.S. (2011) High ionic conductivity P(VDF-TrFE)/PEO blended polymer electrolytes for solid electrochromic devices. *Phys. Chem. Chem. Phys.*, **13**, 13319–13326.
- 67 Jensen, J. and Krebs, F.C. (2014) From the bottom up – flexible solid state electrochromic devices. *Adv. Mater.*, **26**, 7231–7234.
- 68 Jensen, J., Dam, H.F., Reynolds, J.R., Dyer, A.L., and Krebs, F.C. (2012) Manufacture and demonstration of organic photovoltaic-powered electrochromic displays using roll coating methods and printable electrolytes. *J. Polym. Sci., Part B: Polym. Phys.*, **50**, 536–545.

- 69 Søndergaard, R.R., Hösel, M., and Krebs, F.C. (2013) Roll-to-roll fabrication of large area functional organic materials. *J. Polym. Sci., Part B: Polym. Phys.*, **51**, 16–34.
- 70 Polat, E.O., Balci, O., and Kocabas, C. (2014) Graphene based flexible electrochromic devices. *Sci. Rep.*, **4**, 6484.
- 71 Andersson Ersman, P., Kawahara, J., and Berggren, M. (2013) Printed passive matrix addressed electrochromic displays. *Org. Electron.*, **14**, 3371–3378.
- 72 Cui, M., Ng, W.S., Wang, X., Darmawan, P., and Lee, P.S. (2015) Enhanced Electrochromism with rapid growth layer-by-layer assembly of polyelectrolyte complexes. *Adv. Funct. Mater.*, **25**, 401–408.
- 73 Wang, J., Khoo, E., Lee, P.S., and Ma, J. (2008) Synthesis, assembly, and electrochromic properties of uniform crystalline WO₃ nanorods. *J. Phys. Chem. C*, **112**, 14306–14312.
- 74 Wang, J., Khoo, E., Lee, P.S., and Ma, J. (2009) Controlled synthesis of WO₃ nanorods and their electrochromic properties in H₂SO₄ electrolyte. *J. Phys. Chem. C*, **113**, 9655–9658.
- 75 Cai, G., Wang, X., Cui, M., Darmawan, P., Wang, J., Eh, A.L.-S. *et al.* (2015) Electrochromo-supercapacitor based on direct growth of NiO nanoparticles. *Nano Energy*, **12**, 258–267.
- 76 Kim, J., You, J., Kim, B., Park, T., and Kim, E. (2011) Solution processable and patternable poly(3,4-alkylenedioxythiophene)s for large-area electrochromic films. *Adv. Mater.*, **23**, 4168–4173.
- 77 Mortimer, R.J., Dyer, A.L., and Reynolds, J.R. (2006) Electrochromic organic and polymeric materials for display applications. *Displays*, **27**, 2–18.
- 78 Deshpande, R., Lee, S.H., Mahan, A.H., Parilla, P.A., Jones, K.M., Norman, A.G. *et al.* (2007) Optimization of crystalline tungsten oxide nanoparticles for improved electrochromic applications. *Solid State Ionics*, **178**, 895–900.
- 79 Song, Y.-Y., Gao, Z.-D., Wang, J.-H., Xia, X.-H., and Lynch, R. (2011) Multistage coloring electrochromic device based on TiO₂ nanotube arrays modified with WO₃ nanoparticles. *Adv. Funct. Mater.*, **21**, 1941–1946.
- 80 Lee, S.H., Deshpande, R., Parilla, P.A., Jones, K.M., To, B., Mahan, A.H. *et al.* (2006) Crystalline WO₃ nanoparticles for highly improved electrochromic applications. *Adv. Mater.*, **18**, 763–766.
- 81 Devan, R.S., Gao, S.-Y., Ho, W.-D., Lin, J.-H., Ma, Y.-R., Patil, P.S. *et al.* (2011) Electrochromic properties of large-area and high-density arrays of transparent one-dimensional β -Ta₂O₅ nanorods on indium-tin-oxide thin-films. *Appl. Phys. Lett.*, **98**, 133117.
- 82 Park, S.Y., Lee, J.M., Noh, C., and Son, S.U. (2009) Colloidal approach for tungsten oxide nanorod-based electrochromic systems with highly improved response times and color efficiencies. *J. Mater. Chem.*, **19**, 7959–7964.
- 83 Liao, C.-C., Chen, F.-R., and Kai, J.-J. (2007) Annealing effect on electrochromic properties of tungsten oxide nanowires. *Sol. Energy Mater. Sol. Cells*, **91**, 1258–1266.
- 84 Yoo, S.J., Lim, J.W., Sung, Y.-E., Jung, Y.H., Choi, H.G., and Kim, D.K. (2007) Fast switchable electrochromic properties of tungsten oxide nanowire bundles. *Appl. Phys. Lett.*, **90**, 173126.

- 85 Xiong, C., Aliev, A.E., Gnade, B., and Balkus, K.J. (2008) Fabrication of silver vanadium oxide and V_2O_5 nanowires for electrochromics. *ACS Nano*, **2**, 293–301.
- 86 Lin, S.-H., Chen, F.-R., and Kai, J.-J. (2008) Electrochromic properties of nano-structured nickel oxide thin film prepared by spray pyrolysis method. *Appl. Surf. Sci.*, **254**, 2017–2022.
- 87 Cheng, K.-C., Chen, F.-R., and Kai, J.-J. (2007) Electrochromic property of nano-composite Prussian Blue based thin film. *Electrochim. Acta*, **52**, 3330–3335.
- 88 Shim, H.-S., Kim, J.W., Sung, Y.-E., and Kim, W.B. (2009) Electrochromic properties of tungsten oxide nanowires fabricated by electrospinning method. *Sol. Energy Mater. Sol. Cells*, **93**, 2062–2068.
- 89 Manceriu, L.M., Rougier, A., and Duta, A. (2015) Comparative investigation of the Ti and Mo additives influence on the opto-electronic properties of the spray deposited WO_3 thin films. *J. Alloys Compd.*, **630**, 133–145.
- 90 Li, H., Chen, J., Cui, M., Cai, G., Eh, A.L.-S., Lee, P.S. *et al.* (2016) Spray coated ultrathin films from aqueous tungsten molybdenum oxide nanoparticle ink for high contrast electrochromic applications. *J. Mater. Chem. C*, **4**, 33–38.
- 91 Tudorache, M. and Bala, C. (2007) Biosensors based on screen-printing technology, and their applications in environmental and food analysis. *Anal. Bioanal. Chem.*, **388**, 565–578.
- 92 Liu, J. and Coleman, J.P. (2000) Nanostructured metal oxides for printed electrochromic displays. *Mater. Sci. Eng., A*, **286**, 144–148.
- 93 Coleman, J.P., Lynch, A.T., Madhukar, P., and Wagenknecht, J.H. (1999) Printed, flexible electrochromic displays using interdigitated electrodes. *Sol. Energy Mater. Sol. Cells*, **56**, 395–418.
- 94 Coleman, J.P., Lynch, A.T., Madhukar, P., and Wagenknecht, J.H. (1999) Antimony-doped tin oxide powders: Electrochromic materials for printed displays. *Sol. Energy Mater. Sol. Cells*, **56**, 375–394.
- 95 Andersson, P., Forchheimer, R., Tehrani, P., and Berggren, M. (2007) Printable all-organic electrochromic active-matrix displays. *Adv. Funct. Mater.*, **17**, 3074–3082.
- 96 Kawahara, J., Ersman, P.A., Engquist, I., and Berggren, M. (2012) Improving the color switch contrast in PEDOT:PSS-based electrochromic displays. *Org. Electron.*, **13**, 469–474.
- 97 Andersson, P., Nilsson, D., Svensson, P.O., Chen, M., Malmström, A., Remonen, T. *et al.* (2002) Active matrix displays based on all-organic electrochemical smart pixels printed on paper. *Adv. Mater.*, **14**, 1460–1464.
- 98 Pettersson, H., Gruszecki, T., Johansson, L.-H., Edwards, M.O.M., Hagfeldt, A., and Matuszczyk, T. (2004) Direct-driven electrochromic displays based on nanocrystalline electrodes. *Displays*, **25**, 223–230.
- 99 Periyat, P., Leyland, N., McCormack, D.E., Colreavy, J., Corr, D., and Pillai, S.C. (2010) Rapid microwave synthesis of mesoporous TiO_2 for electrochromic displays. *J. Mater. Chem.*, **20**, 3650–3655.
- 100 Calvert, P. (2001) Inkjet printing for materials and devices. *Chem. Mater.*, **13**, 3299–3305.

- 101 Tobjörk, D. and Österbacka, R. (2011) Paper electronics. *Adv. Mater.*, **23**, 1935–1961.
- 102 Möller, M., Asaftei, S., Corr, D., Ryan, M., and Walder, L. (2004) Switchable electrochromic images based on a combined top–down bottom–up approach. *Adv. Mater.*, **16**, 1558–1562.
- 103 Shim, G.H., Han, M.G., Sharp-Norton, J.C., Creager, S.E., and Foulger, S.H. (2008) Inkjet-printed electrochromic devices utilizing polyaniline-silica and poly(3,4-ethylenedioxythiophene)-silica colloidal composite particles. *J. Mater. Chem.*, **18**, 594–601.
- 104 Chen, B.-H., Kao, S.-Y., Hu, C.-W., Higuchi, M., Ho, K.-C., and Liao, Y.-C. (2015) Printed multicolor high-contrast electrochromic devices. *ACS Appl. Mater. Interfaces*, **7**, 25069–25076.
- 105 Costa, C., Pinheiro, C., Henriques, I., and Laia, C.A.T. (2012) Electrochromic properties of inkjet printed vanadium oxide gel on flexible polyethylene terephthalate/indium tin oxide electrodes. *ACS Appl. Mater. Interfaces*, **4**, 5266–5275.
- 106 Wojcik, P.J., Pereira, L., Martins, R., and Fortunato, E. (2013) Statistical mixture design and multivariate analysis of inkjet printed a-WO₃/TiO₂/WO_x electrochromic films. *ACS Comb. Sci.*, **16**, 5–16.
- 107 Wojcik, P.J., Cruz, A.S., Santos, L., Pereira, L., Martins, R., and Fortunato, E. (2012) Microstructure control of dual-phase inkjet-printed a-WO₃/TiO₂/WO_x films for high-performance electrochromic applications. *J. Mater. Chem.*, **22**, 13268–13278.
- 108 Wojcik, P.J., Santos, L., Pereira, L., Martins, R., and Fortunato, E. (2015) Tailoring nanoscale properties of tungsten oxide for inkjet printed electrochromic devices. *Nanoscale*, **7**, 1696–1708.
- 109 Santos, L., Wojcik, P., Pinto, J.V., Elangovan, E., Viegas, J., Pereira, L. *et al.* (2015) Structure and morphologic influence of WO₃ nanoparticles on the electrochromic performance of dual-phase a-WO₃/WO₃ inkjet printed films. *Adv. Electron. Mater.*, **1**, 1400002.
- 110 Yu, J.-S., Kim, I., Kim, J.-S., Jo, J., Larsen-Olsen, T.T., Sondergaard, R.R. *et al.* (2012) Silver front electrode grids for ITO-free all printed polymer solar cells with embedded and raised topographies, prepared by thermal imprint, flexographic and inkjet roll-to-roll processes. *Nanoscale*, **4**, 6032–6040.
- 111 Sagu, J.S., York, N., Southee, D., and Wijayantha, K.G.U. (2015) Printed electrodes for flexible, light-weight solid-state supercapacitors – a feasibility study. *Circuit World*, **41**, 80–86.
- 112 Liu, W., Shi, H., Andersen, T.R., Zawacka, N.K., Cheng, P., Bundgaard, E. *et al.* (2015) Roll-coating fabrication of ITO-free flexible solar cells based on a non-fullerene small molecule acceptor. *RSC Adv.*, **5**, 36001–36006.
- 113 Søndergaard, R.R., Hösel, M., Jørgensen, M., and Krebs, F.C. (2013) Fast printing of thin, large area, ITO free electrochromics on flexible barrier foil. *J. Polym. Sci., Part B: Polym. Phys.*, **51**, 132–136.
- 114 Widjaja, E.J., Delporte, G., Vandeveld, F., and Vanterwyngen, B. (2008) Progress toward roll-to-roll processing of inorganic monolithic electrochromic devices on polymeric substrates. *Sol. Energy Mater. Sol. Cells*, **92**, 97–100.

- 115 Tehrani, P., Hennerdal, L.-O., Dyer, A.L., Reynolds, J.R., and Berggren, M. (2009) Improving the contrast of all-printed electrochromic polymer on paper displays. *J. Mater. Chem.*, **19**, 1799–1802.
- 116 Otley, M.T., Invernale, M.A., and Sotzing, G.A. (2013) Fabric electrochromic displays for adaptive camouflage, biomimicry, wearable displays and fashion, in *Electrochromic Materials and Devices* (eds R.J. Mortimer, D.R. Rosseinsky, and P.M.S. Monk), Wiley-VCH Verlag GmbH & Co. KGaA, pp. 503–524.
- 117 Kang, W., Yan, C., Foo, C.Y., and Lee, P.S. (2015) Foldable electrochromics enabled by nanopaper transfer method. *Adv. Funct. Mater.*, **25**, 4203–4210.

Index

a

- Abbe's diffraction limit 85
- acoustic firing 28
- acoustic principle, droplet formation 29
- acoustic resonators 28
- acrylonitrile butadiene styrene (ABS) 59
- additive manufacturing (AM) *see* 3D printing technologies
- additive RGB (red, green and blue) 320
- additives, organic and inorganic 56
- AFM, spin-coated and printed films 214
- AgNW, at high Ag⁺ concentration 267
- AgNW electrodes, coating method 269
- AgNW network bound, resin 266, 270
- AgNW transparent electrodes
 - bar-coating and spray-coating 266
 - formed from ultra-long 267
 - ITO transparent electrodes 266
 - low sheet resistance and high transparency 266
- air conditioning and mechanical ventilation (ACMV) 319
- Al₂O₃ layer 124
- aluminum oxide (Al₂O₃) nanoparticles 297
- American Chemical Society 192
- ammonium persulfate (APS) 253, 299
- amphiphilic polymers 31
- analyte detection 201
- anodized aluminum oxide (AAO) 253
- apparent interlaminar shear strength (aILSS) 281, 288
- Applied Nanotech 126
- Archimedes principle 239
- Argon 36
- Ar plasma sintering 130
- artificial vapor-sensitive colloidal PCs 201
- atmospheric plasma, jet technologies 37
- atomic force microscopy (AFM) 86
- AuNPs
 - growth, parameters influencing 74
 - high vacuum deposition techniques, AuNPs 70
 - self-assembled 70
 - XRD and HRTE 73
- autocatalytic electroless plating 55
- axisymmetric TCL retraction 199

b

- ball milling 126
- Beer–Lambert law 84
- bioassays 303
- biomedical applications, microdevices 94
- biotinylated C-reactive protein (CRP) antigen 295
- block copolymers 253
- bouncing 185
- Bragg diffraction 197
- breath ammonia monitoring system 299
- Bruggeman model 233

- Building and Construction Authority (BCA) of Singapore 319
- Building Envelope and Façade system (BEFS) 319
- built-in sintering approach 132
- bulk diffusion mechanisms 33
- bulk transport mechanisms
 - densification 33
 - dislocation flow 33
- 2-(2-butoxyethoxy)ethanol 126
- butoxy(ethylacetate) 126
- C**
- cadmium sulfide 198
- cadmium telluride (CdTe) nanocrystals 306
- CAD model 109
- camphorsulfonic acid (CSA) 248
- Canon 27
- cantileverbeam test apparatus 277
- capillary forces 184
- capping dodecylamine 36
- carbon fiber composites, functional polymers
 - interlaminar fracture toughness 279
- mechanical tests
 - DCB test 277
 - SBS test 277
- morphology, printed PMMA and PEG droplets 284
- patterns, PMMA microdroplets 278
- printing and sample preparation
 - pressure cycle 278
 - temperature cycle 278
- carbon nanomaterials
 - CNTs 304
 - graphene oxide
 - commercial inks and sensors 302
 - CVD 303
 - gas detectors, production 303
 - vapor sensor 303
 - MWCNTs 302
 - SWCNTs 302
- carbon nanotubes (CNTs) 120
 - DNA-hybridization 304
 - fabrication 305
 - Nafion-MWCNT sensor 306
 - SDS 305
 - SWCNTs 304
- carboxylic fatty acids 125
- cationic initiators 89
- cationic photoinitiators 89
- centrifugation 126
- cetyltrimethylammonium bromide (CTAB) 253
- chalcogenide nanoparticles 215
- charge density, solid electrochromic device 328
- chemical destabilization techniques 31
- chemical sintering, 35–36
 - desorption, protective layer 132
 - stabilizing molecules, dissolving 132
- chemical vapor deposition (CVD) 94, 303
- chemiresistive hydrogen peroxide sensor 251
- classical DLVO theory 123
 - coffee-ring effect: evaporative flux distribution 194
 - inhomogeneous deposition 193
 - nonuniform patterns 167
 - ring-like morphology 167
 - suppression 186
 - unsymmetrical evaporation 193
- coffee stain effect 6
- complex fabricating process 183
- composite material scaffolds 95
- computer-aided design (CAD) software 2
- conducting polymer nanomaterials
 - polythiophene (Pth) 258
 - PEDOT
 - chemical structure 258
 - properties, synthesis of 258
 - polyaniline nanomaterials
 - applications 250
 - chemical structure 246
 - polypyrrole 251
- conductive inkjet ink 120
- conductive metallic nanoinks, formulation
 - high NPs 125
 - printed electronics 125
- conductive polymers

conductor and semiconductors 298
 PEDOT 302
 polyaniline
 aqueous ammonia leaks 299
 high conductivity 299
 polypyrrole 300
 prussian blue 301
 sensor technology 298
 conductive wiring, mechanical flexibility 265
 contact angle (CA) 183
 contact line pinning 167
 contact printing technologies
 advantage and disadvantage 15
 anilox cylinder 14
 offset printing 14
 continuous wave (cw) 130
 conventional silicon-based semiconductors 215
 conventional sintering method 127
 conventional systems 17
 copper layer, inkjet-printed silver 61
 copper nitrate ($\text{Cu}(\text{NO}_3)_2$) 297
 C-reactive protein (CRP)-antigen 294
 CV *see* cyclic voltammetry (CV)
 cyclic voltammetry (CV) 247
 cyclopentadiene 286

d

DCB test 279
 de-facto standard 27
 destabilization, polyacrylic acid 36
 dibenzylidene acetonates 121
 dicyclopentadiene 286
 dielectric permittivity 38
 dielectric structures and non-selective metallization, MPL 93
 Diels-Alder chemistry 286
 differential scanning calorimetry (DSC) 110
 digital laser processing (DLP) method 135
 digital printing technologies and flooring 2, 27
 dimatix materials printer DMP-2800 70

dimethylformamide (DMF) 74, 162, 186, 278
 dimethyl sulfoxide (DMSO) 71, 72
 “direct-writing” method 134, 245
 disk-like or cap-like ink drops 188
 dodecylbenzene sulfonic acid (DBSA) 299
 dodecyltrimethylammonium bromide (DTAB) 253
 donor–acceptor-type electrochromic polymers 323
 dopamine (DA) 253
 doping 247
 double printing process 133
 drop-on-demand (DoD) systems 27
 inkjet printing 119
 droplet coalescence process 191
 droplet formations
 donor layer characteristics 11
 laser parameters 11
 drying, wet sintering
 agglomerates, formation 34
 Marangoni flows 34
 time limiting 34
 dynamic droplet configurations, liquid phase fluid 236
 dynamic release layer (DRL) 269
 dynamic wettability, substrates 190

e

EC materials
 anodic 317
 cathodic 317
 ecoflex substrate 269
 electrical conductivity, polyaniline polymer, oxidation state 247
 protonation level *see* doping
 electrical properties, printed patterns 120
 electrical resistivity 127
 electrical sintering
 AC field, mobile electrodes 132
 DC electrical current 131
 electrochemical deposition 322
 electrochemical polymerization 322
 electrochemical properties, polyaniline 246

- electrochemical sensing 70
 - electrochromic devices (ECD) 317
 - electrochromics (EC) 317
 - displays 320
 - green buildings 318
 - printing techniques
 - flexographic printing 329
 - inkjet printing 326
 - roll-to-roll printing 329
 - screen printing 324
 - solution processing of 322
 - transform, paper quality display technology 320
 - electrode array 64
 - electro-explosion, metal wire 121
 - electrohydrodynamic atomization inkjet printing 297
 - electroless copper 64
 - electroless CuCo alloy, inkjet-printed seed 63
 - electroless deposition (ELD) 52, 55 *see also* electroless plating
 - electroless metal 64
 - electroless plating
 - combining, with printing 52
 - highly selective 55
 - MST 54
 - NST 54
 - on printed parts
 - electroless metal integration 60
 - methods 59
 - printing catalysts 57
 - printing methods
 - with laser processing 53
 - with nanoparticle activated surfaces 53
 - processes 119
 - seed layer printing 57
 - selectivity 54
 - thermodynamics characteristics 56
 - electroluminescent (EL) devices 136
 - electromagnetic (EM) radiation 37
 - electromagnetic sintering approaches 37
 - electromagnetic spectrum 39
 - electroplating 51
 - electrosteric stabilization 124
 - encapsulated liquid crystals (NCAP) 319
 - energy dispersive X-ray spectroscopy (EDS) 73
 - ethanol cooling vs. air cooling printings 239
 - ethylene glycol 187
 - evaporation-condensation 33
 - evaporation processes, inkjet-printed graphene films 170
 - exfoliation solvent 163
 - experimental procedure, 3D structure fabrication 87
- f**
- fabrication time, reduction 77
 - face-centered cubic (fcc) structure, gold 73
 - falling molten droplets 238
 - ferrocene methanol (FeMeOH) 302
 - filamentary printing method 119
 - fluorescence and optical microscopy image, PC12 cells 257
 - free-radical photopolymerization mechanisms 85
 - Frenkel model predictions 113
 - frustum, cone structure 237
 - FujiFilm Dimatix Material Printer 166
 - full-color reflective electrochromic display 321
- g**
- galvanic displacement 55
 - Gentex Corporation 318
 - Gibbs-Thomson equation 33
 - G_{Ic} comparison, non-printed samples and samples 281
 - $G_{Ic(\text{initiation})}$ and $G_{Ic(\text{propagation})}$, printed film samples 281
 - glass reinforced epoxy 58
 - glass transition temperatures 31
 - glucose oxidase (GOx) 249
 - gold nanoink sintering, glass substrates 130
 - gold nanoparticles (Au NPs) 70, 294
 - grain-boundary energies 33

- graphene and 2D material, thin film printing
 - performance and applications 172
 - printing procedures 162
- graphene monolayer transparent electrodes 267
- graphene nanosheets 176
- graphical applications 27
- h**
 - Hamaker constant 123
 - Hansen solubility parameters 162
 - height-diameter ratio (H/D) 197
 - heterocoagulation 30
 - Hewlett Packard 27
 - high-aspect-ratio AgNW networks 267
 - high resolution SEM (HRSEM) 72
 - high-resolution X-ray diffraction (XRD) 73
 - high speed sintering (HSS)
 - case study 115
 - high volume manufacturing 113
 - inkjet benefits 116
 - machine setup & parameter control 109
 - materials & properties 112
 - Nylon 12, 112
 - RAM 109
 - high-vacuum technologies 1
 - high-viscous inkjet system 11
 - high volume manufacturing technology 116
 - horse radish peroxidase (HRP) 249, 295
 - HSS, high volume manufacturing 114
 - hybrid materials 90
 - hydrogen peroxide (H₂O₂) sensor 251
 - hydrophilic substrate 189
 - hydrophobic substrate 189
- i**
 - impulse light sintering 39
 - industrial inkjet
 - acoustic phenomenon 28
 - jettable fluids, values 28
 - Rayleigh type droplet formation 30
 - inertial force, dominates impact process 184
 - injection molding, cost analysis 108
 - injection needle array 240
 - ink droplets, generation process 184
 - ink formulations
 - binder-containing inks 163
 - binder-free inks 162
 - colloidal particles, solvents 186
 - monomer polymerization rate 188
 - multiple components 186
 - inkjet inks
 - nanoparticle inks 30
 - precursor inks 30
 - inkjet printing (IJP)
 - carbon fiber composites, functional polymers
 - mechanical tests 276
 - printing and sample preparation 277
 - patterns, PMMA microdroplets 278
 - patterns, PMMA, PEG microdroplets 283
 - conducting polymer nanomaterials 245
 - deposition technique 184
 - drying process 8
 - electrostatic 10
 - fine controlled PC dots and lines
 - coffee-ring effect, suppression 193
 - substrate wettability 188
 - industrial inkjet, 28–30
 - metallic nanoinks, conductive 2D and 3D structures 119
 - PCs 183
 - piezoelectric IJP 7
 - thermal IJP 7
 - toward 3D printing 10
 - ink preparation method 164
 - ink rheology 5
 - ink stability 4
 - Innovative Manufacturing and Construction Research Centre (IMCRC) 115

inorganic dielectrics, high dielectric constant 221
 inorganic–organic hybrid dielectrics 220
 inorganic semiconductors 215
 intense light processing 40
 interfacial jamming, particles 191
 interfacial transport mechanisms 33
 interlaminar fracture toughness 283
 interlaminar shear strength, composite samples 277
 intrinsically conducting polymer 246
 intrinsic repair of composites, printed polymers 286
 intrinsic roll-to-roll processes 14
 ion-gel dielectrics 220
 IR sintering 130
 N-isopropyl acrylamide are 188

j

jetting and patterns 166
 Joule heating effect 235

k

kinetic energy, deformation energy conversion 185
 Kruss EasyDrop 71

l

laser annealing process, films 172
 laser-array exposure 17
 laser-induced forward transfer (LIFT) 1, 265
 laser metal deposition (LMD) 229
 laser sintering (LS) 111
 laser beam focus 130
 latex suspensions 197
 layer-by-layer manufacturing
 technology *see* 3D printing technologies
 leucoemeraldine 246
 Li-doped ZnO, transfer characteristics 217
 LIFT, droplet formation 11
 light-emitting diode (LED) 137, 270
 liquid crystal (LC) 318
 liquid metal printing ink

medical electronics 230, 232
 metal bone cement 231, 232
 other materials of 231, 233
 physical properties of 230, 231
 TEM image of 231
 liquid phase 3D printing
 fabrication scheme 234
 future liquid phase printing 240
 liquid phase cooling fluid 234
 liquid phase cooling vs. gas phase cooling 238
 metal objects, in cooling liquid 235, 236
 metal structures 236
 printing quality 237
 lithographic techniques 93
 low-adhesive superhydrophobic substrate 190
 low and high concentration, wet air 202
 low cost mass production, electronic devices 121
 low evaporation temperature 195
 low melting point metal ink, liquid metal printing ink 230
 low thermal-annealing temperatures 215

m

Marangoni flow 186, 195
 materials for MPP
 hybrid materials 90
 organic photopolymers 89
 SU-8 90
 mechanical stirring 126
 mechanical tests
 DCB test 277
 SBS test 277
 metal ion printing 57
 metal-based inks, conductive applications
 chemical sintering, 35–36
 drying, wet sintering, 34–35
 microwave sintering 40
 nanoparticles or clusters 30
 sintering, electro-magnetic fields, 37–39

- sintering, mechanisms, 32–34
- thermal sintering 35
- metal/electrolyte couple 55
- metallic inkjet nanoinks, printed
 - electronics
 - RFID tag 136
 - TFT 136
- metallic inks
 - conductivity nanoparticle materials 294
 - copper, nickel, alumina 296
 - gold
 - HRP 294
 - nanoparticle arrays 295
 - metal oxide 298
 - polymer, surfactant coatings 294
 - silver
 - fabricate devices and electronics 296
 - highly conductive 296
 - humidity sensors 296
- metallic nanoinks, conductive 2D and 3D structures
 - requirements, challenges 120
 - stabilization, metal NPs 122
 - synthesis, metal NPs 121
- metallic nanoparticles 294
- metallization – dipping 61
- metal NPs
 - stabilization
 - against aggregation 122
 - against oxidation 124
 - synthesis
 - bottom-up approach, formed from precursor ions 121
 - bulk metal, breaking of 121
 - high energy radiations 122
 - organometallic compounds 121
- metal oxide nanoparticles 298
- metamaterials 93
- metal 3D printing
 - electronic manufacturing of 229
 - LED circuit 229, 230
- micelles 253
- microcolloidal crystals, controllable 3D morphology 199, 200
- microcontact printing 14
- MicroFab Inc. 278
- microfluidic, biomedical structures 90
- micro-scaffold 95
- micro system technology (MST) 54
- micro-supercapacitors (mSCs)
 - Kapton, graphene electrodes 175
 - planar 173
- microwave flash method 298
- microwave sintering 40, 131
- mixed cellulose ester membrane 296
- modified ink with additives 57
- molten metal ink, inject 240
- monodispersed particles 186
- monolayer graphene sheet 269
- monomer/oligomer 89
- monomer, polymer conversion 88
- monomer polymerization rate 188
- MoS₂ device 175
- MPP materials, photoinitiators 88
- multi-functional EC device 321
- multi-layered electrochromic display 321
- multi-material stack 41
- multi-photon absorption (MPA) 84
- multiphoton lithography (MPL) 83
- multiphoton polymerization, 3D printing
 - applications 91
 - diffraction limit 85
 - experimental set-up 86
 - MEMS 83
 - microfluidics 83
 - MPA 84
 - MPP materials 88
 - photosensitive materials 83
- multi-walled CNTs (MWCNTs) 302
- MWCNT-NP's inkjet-printed sensor 307

n

- NanoChromics™ technology 320
- nano liquid metal fluid 232
 - different nano particles 233, 234
 - thermal conductivity 233
- nanomaterials and nanocomposites, sensor fabrication
 - carbon nanomaterials 302

- nanomaterials and nanocomposites,
 - sensor fabrication (*contd.*)
 - conductive polymers 298
 - metallic inks, gold 294
 - metal oxide, silver 296, 297
- nanometer-scale WO_3 nanoparticles 298
- nanoparticles (NPs) 120
- nanosystem technology (NST) 54
- nanowires (NWs) 120
- National Climate Change Secretariat of Singapore (NCCS) 319
- near-field scanning optical microscopy (NSOM) 86
- neck growth 31
- negative refractive index 93
- nicotinamide adenine dinucleotide (NADH) 302
- N*-methyl-2-pyrrolidone (NMP) 162, 250, 296
- noncontact printing 1
- nonionic amphiphiles 298
- non-light patterning techniques 86
- normalized conductance current versus electrochemical potential 248
- NovaCentrix (USA) 126
- novel techniques 34
- nozzle-based printing 213
- nucleotides 253
- numerical aperture (N.A.) 86
- o**
 - optical microscopy images 267
 - optical parametric oscillator (OPO) 86
 - organic solar cells (OSC) 119
 - metallic electrode 139
 - photovoltaic devices 138
- p**
 - palladium (Pd) ions 57
 - 2015 Paris Climate Conference 317
 - PC microchip, hydrophilic PC dots 203
 - PC patterning methods 183
 - PC patterns
 - filtration 196
 - fluorescent PC 198
 - H/D ratio 198
 - PC dots or lines 196
 - photo-annealed IGZO TFT 219
 - photodetectors 175
 - photoinitiators
 - high two-photon cross-section 89
 - laser wavelength 88
 - photolithography 119
 - photoluminescent GO nanosheets 304
 - photonic and microwave flash
 - treatments 131
 - photonic crystals (PCs)
 - applications, printing 196
 - IJP, fine controlled PC dots and lines
 - ink formation 186
 - substrate wettability 188
 - light manipulation properties 183
 - patterned 183
 - process, inkjet printing 184
 - photonic flash sintering
 - intense light pulse 129
 - R2R processing 129
 - photonic metamaterials 93
 - photonic sintering 41
 - excitation wavelengths 129
 - selective light absorption 129
 - photopolymerization 84
 - optical manufacturing technology 17
 - photocurable materials 18
 - vat photopolymerization 17
 - photopolymer ORMOCER 91
 - photosensitive polymer 87
 - physical, vacuum deposition (PVD) 57
 - piezo-actuation frequencies 29
 - piezo-based inkjet technologies 27
 - plasma ashing 71
 - plasma sintering printed patterns, to
 - low-pressure 130
 - Plateau-Rayleigh instability 10, 28
 - PMMA *see* poly(methyl methacrylate) (PMMA)
 - pneumatic-typed fused deposition
 - modeling 238
 - polarized piezo-ceramics 28
 - poly(3,4-ethylenedioxythiophene) (PEDOT) 302

- chemical structure 258
- properties, synthesis of 258
- poly(acrylic acid) (PAA) shell 124, 196
- polyaniline 246
- polyaniline-copper chloride (CuCl_2)
nanocomposites 300
- polyaniline nanomaterials
 - chemical structure 246
 - applications 250
 - inkjet printed 249
- polyaniline-poly(4-styrenesulfonate)
(PANI-PSS) 250
- polyaniline synthesis
 - chemical oxidative polymerization 248
 - electrochemical polymerization 248
- polyaniline with dodecylbenzene
sulfonic acid (PANI-DBSA) 323
- polycarbonate (PC) 39
- polycarboxylate salts 322
- polycation
 - poly(diallyldimethylammonium
chloride) (PDAC) 132
- polydimethylsiloxane (PDMS)
electrodes 269
- polyelectrolyte multilayers (PEMs) 60
- polyethylene glycol (PEG) 278
- poly(ethylene glycol) diacrylate
(PEGDA) matrix 134
- poly(ethylene naphthalate) (PEN) 39
- polyethylene terephthalate
(PET) 39, 301
- polymer-dispersed liquid crystals
(PDLC) 319
- polymeric electrochromes
 - π -conjugated 322
 - transmissive/reflective ECs and
displays 322
- poly(methyl methacrylate) (PMMA)
220, 278
- polyols 124
- polypyrrole (Ppy) 301
 - cyclic voltammogram 252
 - electroactive polymer 252
 - inkjet printing and applications 254
 - nanoformulations 253
 - properties and synthesis of 251
 - SEM images 254
- polystyrene (PS) 220
- polystyrene sulfonate (PSS) 250, 302
- polytetrafluoroethylene (PTFE) film
277
- polythiophene (Pth)
 - chemical structure 258
 - inkjet printing and applications 258
 - properties, synthesis of 258
- polyvinylpyrrolidone (PVP) 35, 123,
267
- porous aluminosilicate 253
- positive photoresists, MPL 93
- powder bed fusion (PBF) 19
- powder bed technology 19
- presintering 40
- primary thermodynamic driving force
33
- printable dielectric materials
 - dielectrics, high capacitance 220
 - inorganic-organic hybrid dielectrics
220
 - ionic liquid and triblock copolymer
221
 - passive materials, active device 219
- printable semiconducting materials
 - bandgap 213
 - cyclopentasilane 215
 - electrical stability 215
 - field-effect mobility 214
 - organic semiconductors 213
 - synthetic approaches 218
- printed AgNW electrodes
 - AgNWs printing, LIFT 269
 - fabrication and properties, stretchable
electrodes 269
- printed array, heat treatment 78
- printed films, gellan gum 306
- printed graphene transparent
conductive films 173
- printed parts, electroless plating
 - electroless metal integration 60
- methods
 - preseed surface modification 60
 - printed Ag ink 60
 - printed Pd seed 59

- printed polyaniline films 301
- printed silver nanowires, laser-induced forward transfer
 - AgNW transparent electrodes 266
- printed AgNW electrodes
 - AgNWs printing, LIFT 269
 - fabrication and properties, stretchable electrodes 269
- printhead technologies, employ ink flow 30
- printing PCs, applications in chemical detection 201
 - microcolloidal crystals, controllable 3D morphology 199
 - PCs patterns 196
 - in vapor sensors 201
- printing procedures
 - drying 166
 - ink formulations 162
 - jetting and patterns 167
 - posttreatments
 - graphene flakes 172
 - insulating 171
- printing techniques, EC
 - fabricate electrochromic device 329
- flexographic printing 329
- inkjet printing
 - digital printing method 326
 - electrochromic cell, silver grid electrode 328
 - non-contact direct write technology 326
- roll-to-roll printing 329
- screen printing
 - additive patterning method 324
 - flat printing technique 324
 - high viscosity, low volatility 324
 - PEDOT, PSS based active-matrix display 325
- printing technologies, nanomaterials
 - contact printing technologies 13
 - gravure printing 15
 - ink formulation strategies 4
 - inkjet printing 7
 - LIFT 11
 - photopolymerization 17
 - powder bed technology 19
 - properties, 2D materials 166
 - 3,4-propylenedioxythiophene (ProDOT), switches 322
 - prussian blue 301
 - p-type organic semiconductors 214
 - PVP capping agent, sheet resistance 268
- q**
 - quenching 86
- r**
 - radiation absorbing material (RAM) 109
 - radical photoinitiators 89
 - RAM 110, 112
 - Rayleigh instability 192
 - reactive inkjet (RIJ)
 - Au NPs growth, parameters influencing 74
 - chemical patterning approach 69
 - fabrication time, reduction 77
 - printing scheme 71
 - printing techniques 69
 - self-assembled Au NPs 70
 - single cartridge step 77
 - real-time optical microscope images 202
 - recrystallisation 111
 - reducing agent/electrolyte couple 55
 - reductive (H_2) atmospheres 128
 - reversible electrochemical mirrors (REMs) 321
 - reversible electrodeposition 321
 - rheological measurements 29
 - rheology 119
 - ribbon-and wire-like nanostructures 253
 - ring-like deposition 186
 - roll-to-roll (R2R)
 - printing 213
 - technique 120
 - Royal Society of Chemistry 203
 - R2R printing, heat-sensitive flexible substrates 121
 - RT sintering 132

- Ruffo model 114
- ruthenium-based dye-sensitized solar cells 176
- S**
- saturated calomel electrode (SCE) 253
- scanning electron microscope (SEM) 249
- screen printing
 - conductive films 119
 - embodiments of 16
- seed layer printing
 - metal ion printing 57
 - printing nanoparticle ink 57
- self-assembled monolayer (SAM) 60
- self-diffusion, surface atoms 127
- SEM image
 - AuNPs 74, 76
 - 2D conductive structures 128
- sensors, automotive safety 293
- sequential absorption 84
- sheet resistance, optical transmittance 127, 268
- sheet-to-sheet/roll-to-roll compatibility 39
- short beam shear (SBS) 276
- silver-based EC 321
- silver nanowires (AgNWs) 265
- simultaneous absorption 84
- single cartridge step 77
- single-walled carbon nanotubes (SWCNT) 253, 302
- sintering, mechanisms
 - Arrhenius-type behavior 32
 - bulk transport 33
 - Gibbs-Thomson equation 33
- smart windows technology
 - EC 318
 - LC 318
- sodium dodecyl benzene sulfonate (SDBS) 256
- sodium dodecyl sulfate (SDS) 123, 305
- soft-template methods 253
- solar cells 177
- solar heat gain coefficient (SHGC) 318
- solution-casting polymerization 322
- solution-processable coating techniques
 - hydrothermal, solvothermal 322
 - spray-coating, slot-die coating 322
- solution processing, EC
 - polymeric electrochromes 322
 - solution-processable coating techniques 322
- spiral electrodes, jetted poly(3-hexylthiophene) polymer 259
- splashing 185
- spreading 185
- stabilization
 - against aggregation
 - agglomeration and sedimentation 122
 - electrostatic 123
 - against oxidation
 - oxidation, Cu NPs 125
 - silver NPs 124
 - transmetallation 125
 - steric 123
- stereolithography 108
- stöbersynthesis 186
- substrate wettability
 - hydrophilic or hydrophobic 188
 - morphology 188
- substrate-catalyzed electroless plating 55
- substrate, influence, 41–42
- subtractive CMY 320
- superhydrophobic substrate 190
- supply chain, opening 115
- supramolecular protein layers
 - streptavidin 295
- surface diffusion 33
- surface energy, kinetic energy
 - conversion 185
- surface topography 172
- surface-to-volume ratio 127
- surfactant sodium dodecylsulfate (SDS) 253
- suspended-particle
 - devices (SPD) 318
- synthesis route, monomers 287
- t**
- template-free synthesis 253
- tension gradient 186

- terpineol 164
 - thermal conductivity, volume fraction 234
 - thermal equilibrium 41
 - thermal evaporation/sputtering 70
 - thermal sintering 35
 - heating printed pattern 127
 - necks formation 128
 - thin film transistors (TFT) 136, 245
 - 3D conductive patterns, formation and sintering
 - additive manufacturing 134
 - UV-curable inks, monomers 134
 - UV-curable liquids 134
 - UV-polymerizable oil-in-water emulsion 135
 - 3D metal printing 53
 - 3D morphology, microcolloidal PC pattern 200
 - 3D photonic crystal 92
 - 3D polymer printing 53
 - 3D printing technologies
 - CAD 2
 - selective deposition techniques
 - fused deposition modeling 3
 - viscous jetting 3
 - 3D printed substrate 62
 - three phase contact line (TCL) 185
 - time-dependent model 41
 - Ti, Sapphire femtosecond oscillator 86
 - TNO 10
 - top-contact/bottom-gate OFET device 220
 - top-down patterning approaches 245
 - Toppare group 323
 - transition metal oxide (TMOs) 323
 - transmittance spectra, solid
 - electrochromic device 328
 - transparent and stretchable electrodes, AgNWs 265
 - transparent conductive electrodes (TCE) 119, 317
 - ITO 137
 - ultrathin films formation 137
 - transparent conductors 173
 - transparent electrodes, performance 266
 - Triton X-100 (poly(oxyethylene)octyl phenyl ether) 123
 - tungsten trioxide (WO_3) films 317
 - 2D metallic structure 129
 - 2D printed pattern, high electrical conductivity 127
 - 2D printing technologies, functional nanomaterials
 - contact (mask-based) printing technologies 1
 - noncontact (maskless) printing technologies 1
 - two-phase organic solvent-water system 124
 - two-photon absorption (TPA)
 - sequential 84
 - simultaneous 84
- u**
- UK Technology Strategy Board 107
 - ultra-long AgNWs 268
 - ultrasonication 126
 - ultraviolet (UV) 37
 - under-the-bonnet applications 107
- v**
- vacuum-deposited oxide
 - semiconductors 215
 - vacuum deposition 119
 - van der Pauw resistivity 63
 - van der Waals interactions 303
 - VOC sensor array 259
 - volatile organic compound (VOC) 258
- w**
- waveform tuning 7
 - wet chemical approach 121
 - whilst laser sintering 113
 - wide-to grand-format printing 27
 - WO_3 nanorods 323
- x**
- x - y galvanometric mirror scanner 86
- y**
- Young's modulus 200
 - Y-shape PC microfluidic immune assay 202

Z

- zero-dimensional objects 4
- zero pressure boundary condition 28
- zero velocity boundary condition 28
- zirconium-doped aluminum oxide
(ZAO) 223
- zirconium doping 223
- Zn-hydroxide precursor, ZnO
semiconductor 216
- ZnO TFTs, ion-gel gate insulator 222
- Zr-doped AlO_x dielectrics 221